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(54) **PROCESSES FOR MAKING SURFACTANTS VIA ADSORPTIVE SEPARATION AND PRODUCTS THEREOF**

(76) Inventors: **Daniel Stedman Connor**, The Procter & Gamble Company, Miami Valley Laboratories P.O. Box 538707, Cincinnati, OH (US) 45253-8707; **Jeffrey John Scheibel**, The Procter & Gamble Company, Miami Valley Laboratories P.O. Box 538707, Cincinnati, OH (US) 45253-8707; **James Charles Theophile Roger Burckett-St. Laurent**, The Procter & Gamble Company, Miami Valley Laboratories P.O. Box 538707, Cincinnati, OH (US) 45253-8707; **Thomas Anthony Cripe**, The Procter & Gamble Company, Miami Valley Laboratories P.O. Box 538707, Cincinnati, OH (US) 45253-8707; **Kevin Lee Kott**, The Procter & Gamble Company, Miami Valley Laboratories P.O. Box 538707, Cincinnati, OH (US) 45253-8707; **Phillip Kyle Vinson**, The Procter & Gamble Company, Miami Valley Laboratories P.O. Box 538707, Cincinnati, OH (US) 45253-8707

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

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(86) PCT No.: **PCT/US99/20124**

§ 371 (c)(1),
(2), (4) Date: **Feb. 28, 2001**

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PCT Pub. Date: **Mar. 9, 2000**

(51) **Int. Cl.**

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C07C 7/13	(2006.01)
C07C 5/333	(2006.01)
C07C 9/16	(2006.01)

(52) **U.S. Cl.** **510/505**; 568/338; 568/361; 568/366; 568/579; 568/882; 568/909

(58) **Field of Classification Search** 568/338, 568/361, 366, 579, 882, 909; 510/505
See application file for complete search history.

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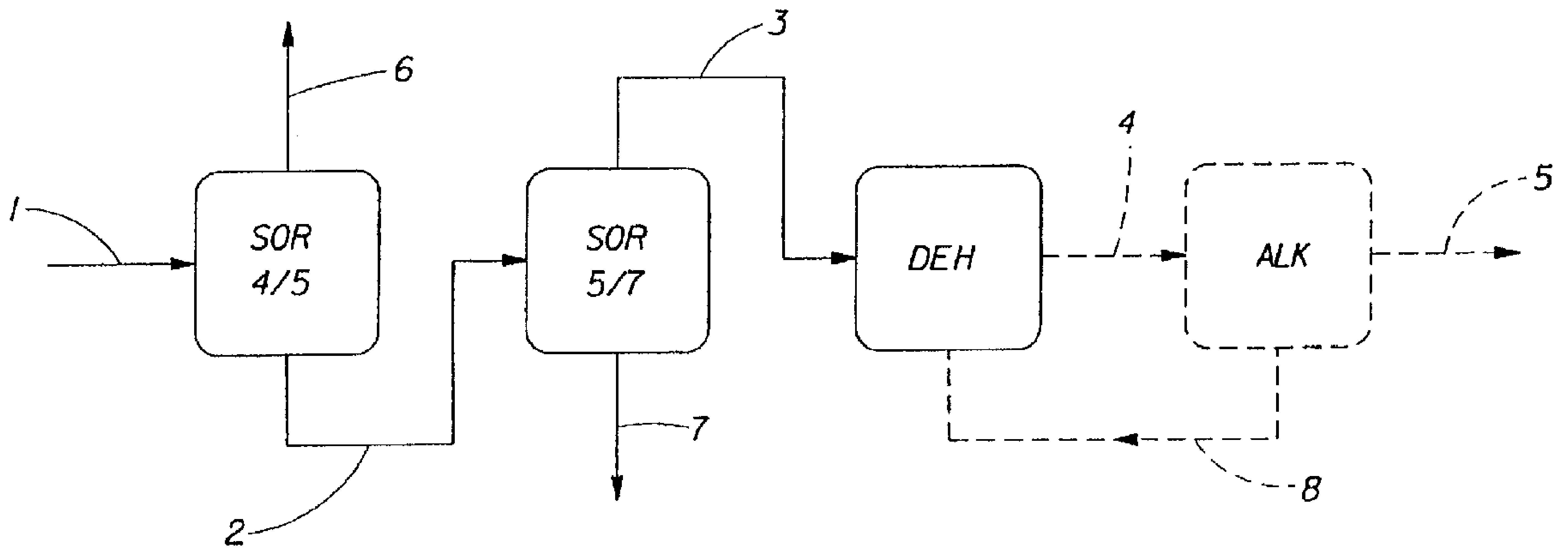
Primary Examiner—Brian P. Mruk

(57) **ABSTRACT**

Processes for making particularly branched, especially monomethyl-branched or nongeminal dimethyl-branched surfactants used in cleaning products; preferred processes comprising particular combinations of two or more adsorptive separation steps and, more preferably, particular OXO and/or alkylation steps; products of such processes, including certain modified primary OXO alcohols and/or alkylbenzenes, modified primary OXO alcohol-derived alkoxylated alcohols, alkylsulfates and/or alkoxysulfates; alkylbenzensulfonate surfactants, and consumer cleaning products, especially laundry detergents, containing them. Preferred processes herein more specifically use specific, unconventional sequences of sorptive separation steps to secure certain branched hydrocarbon fractions which are used in further process steps to make olefins useful in OXO processes or as alkylating agents for arenes or for other useful surfactant-making purposes. Surprisingly, such fractions can even be derived from effluents from current linear alkylbenzene manufacture.

18 Claims, 18 Drawing Sheets



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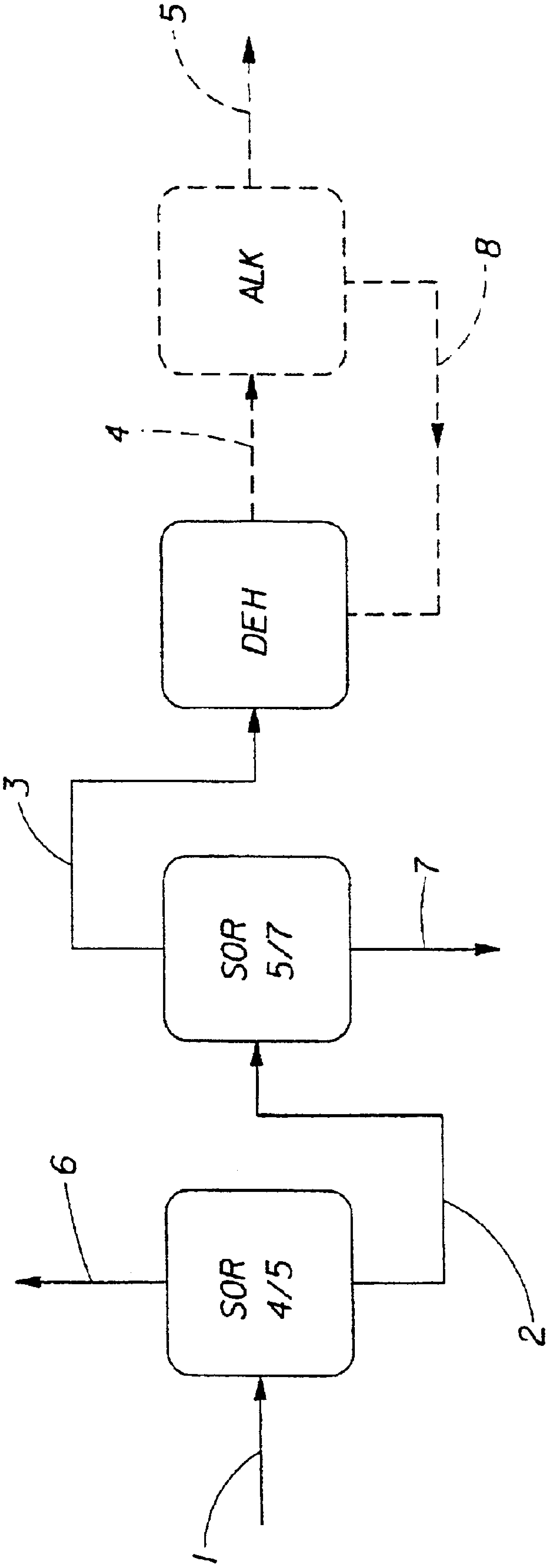

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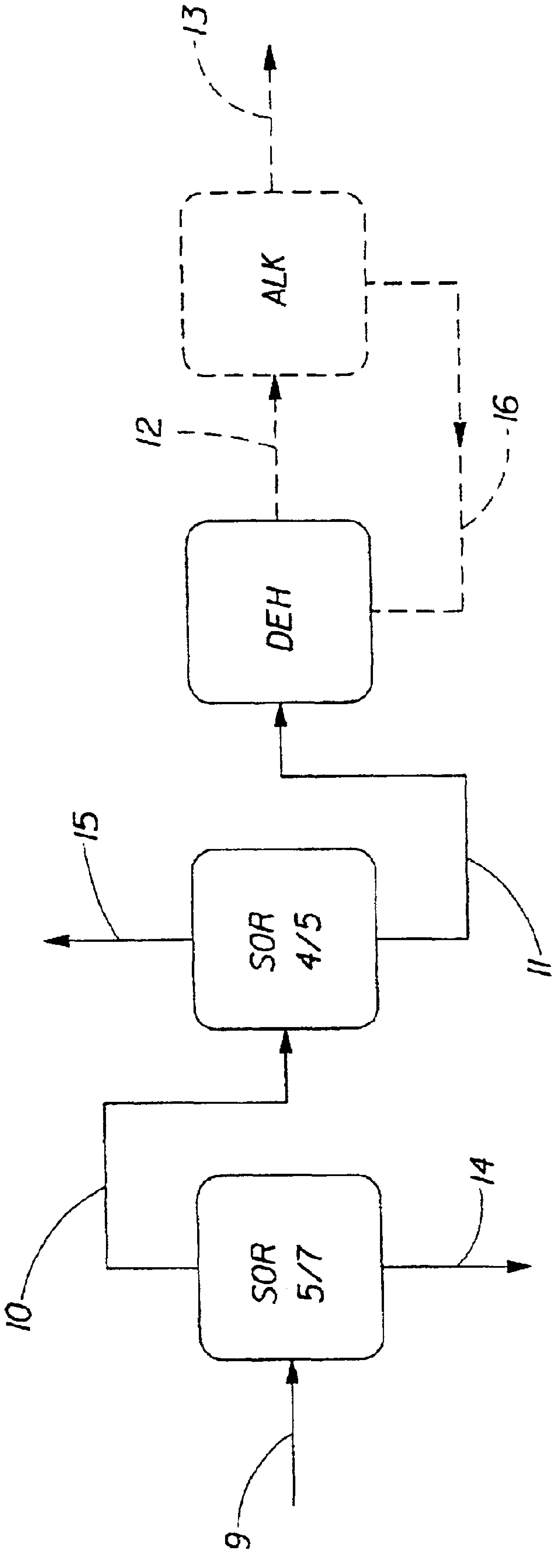

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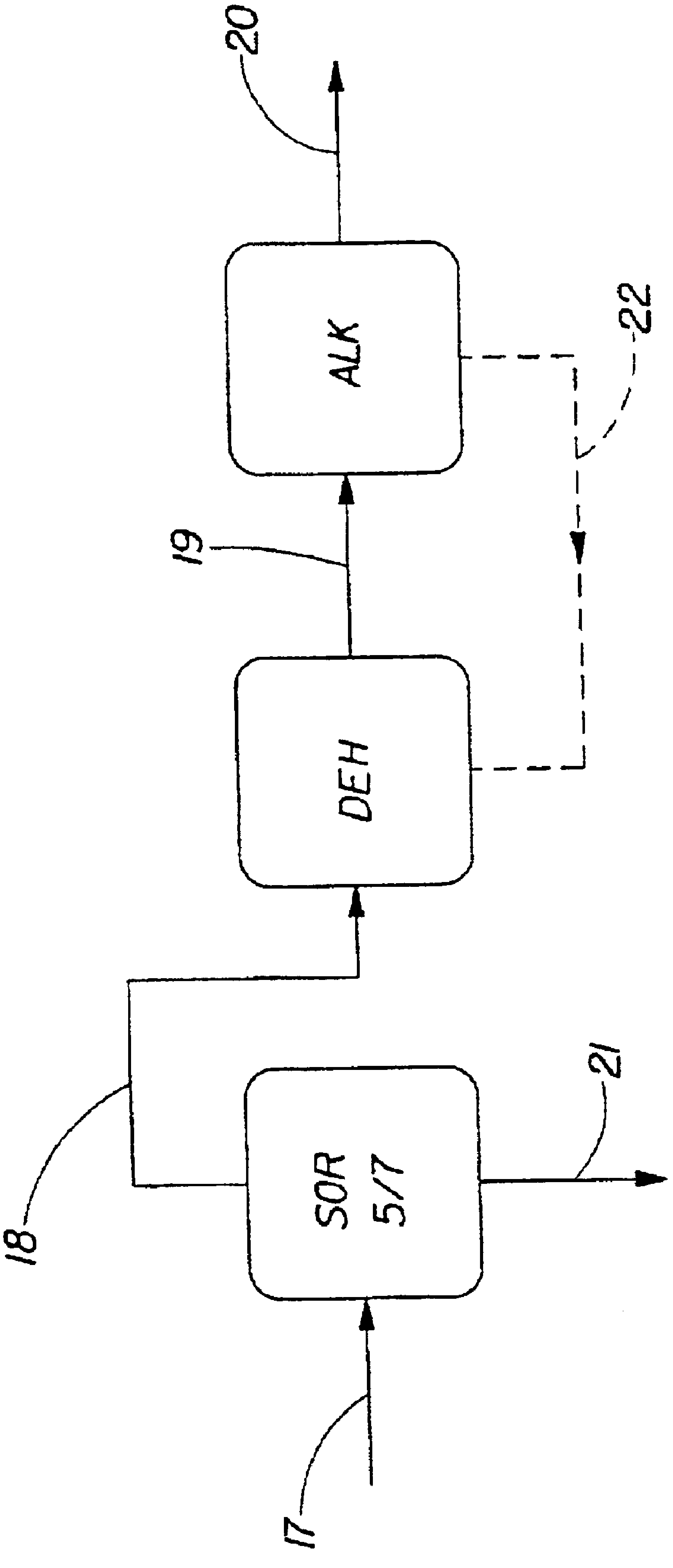

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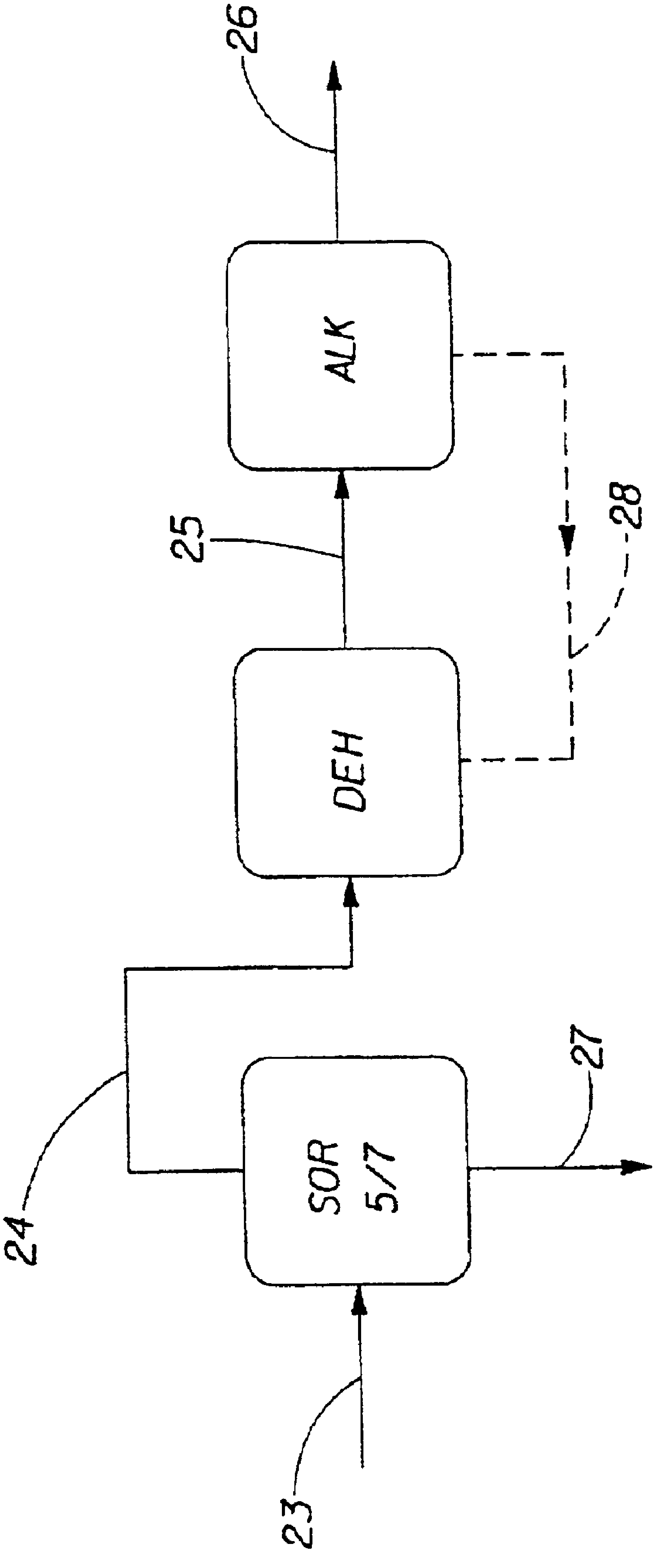

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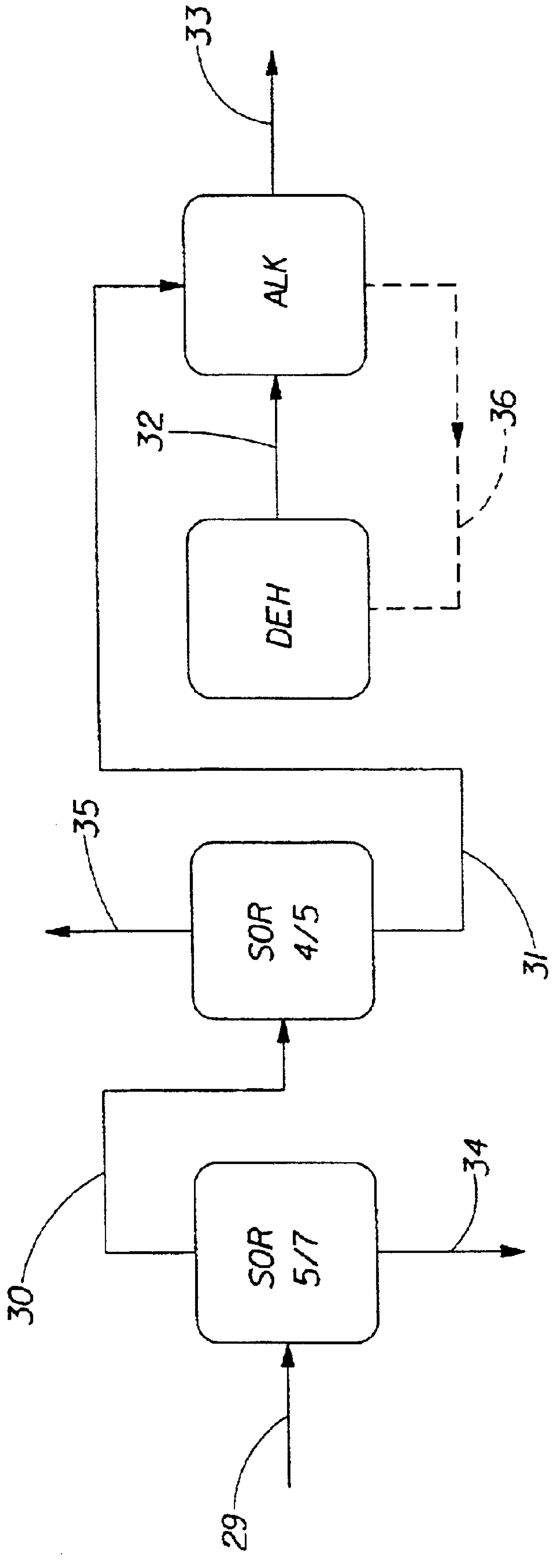

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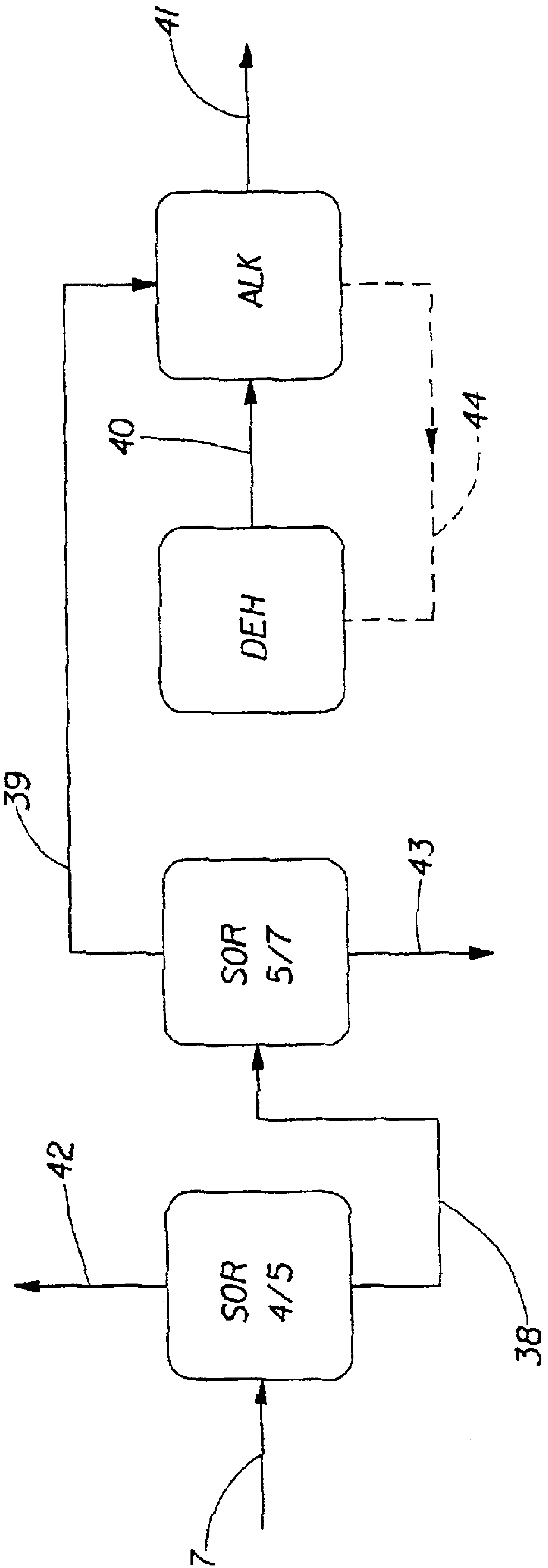

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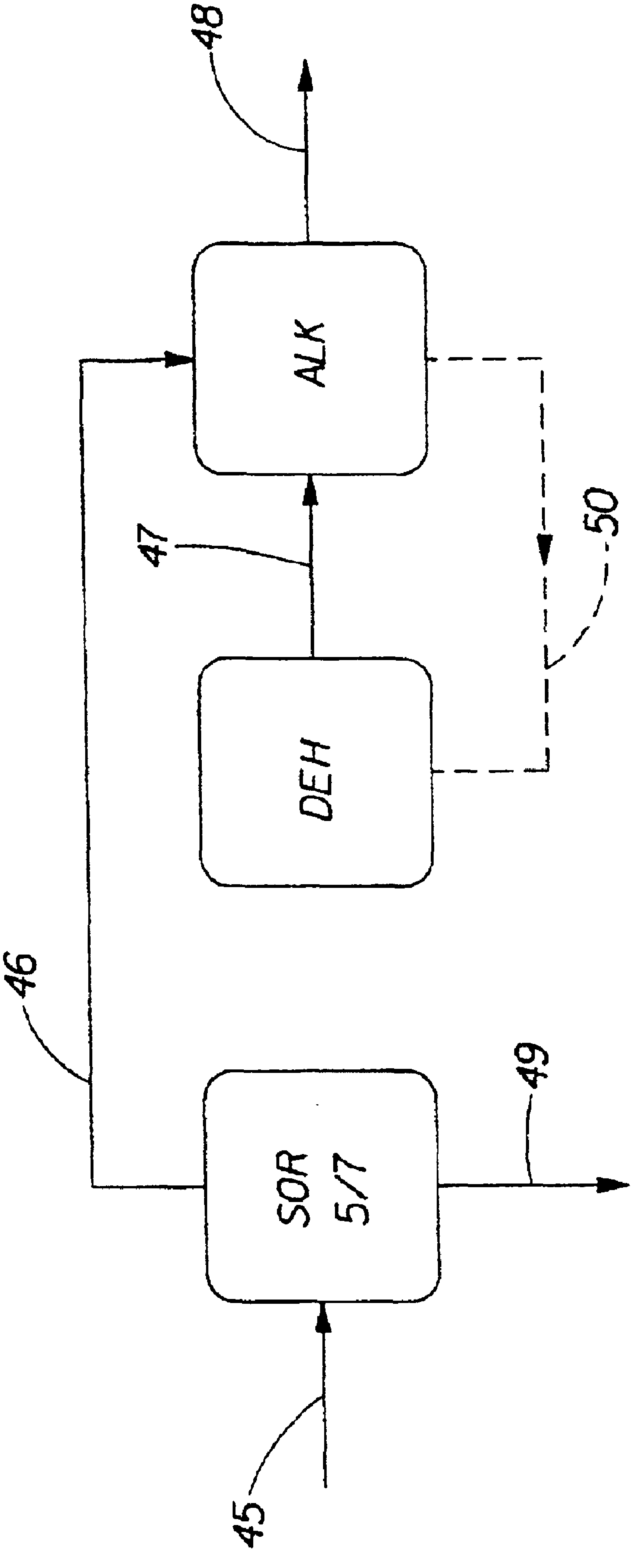

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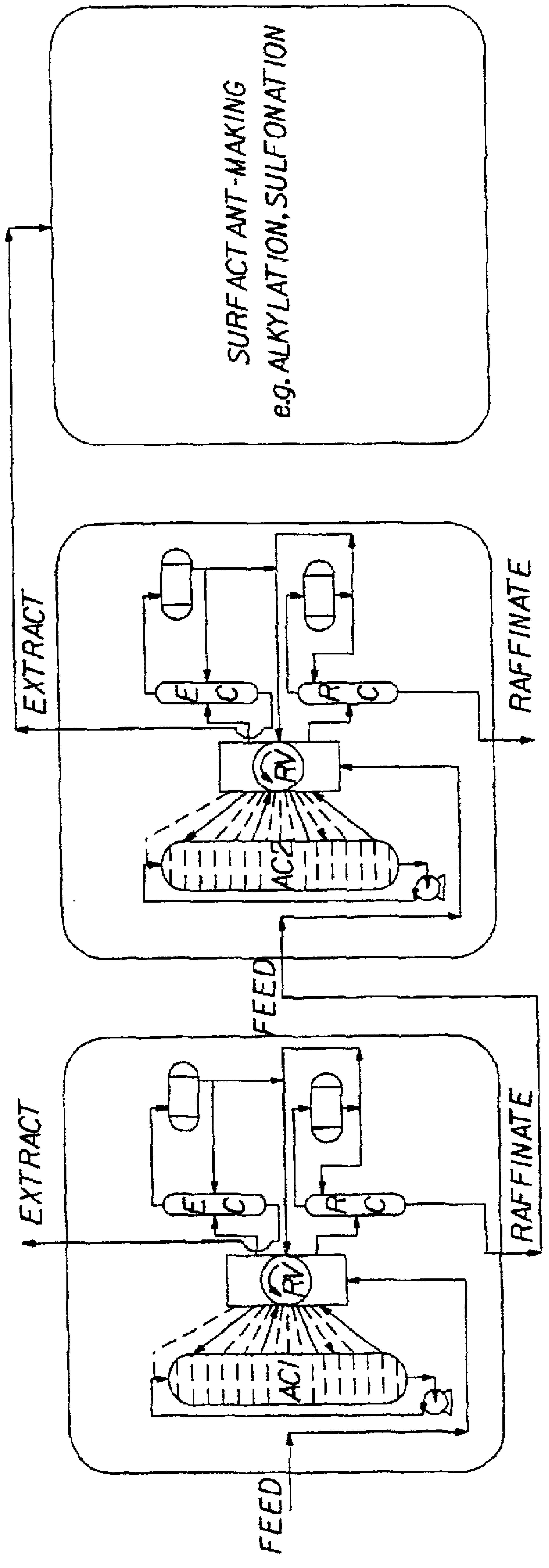
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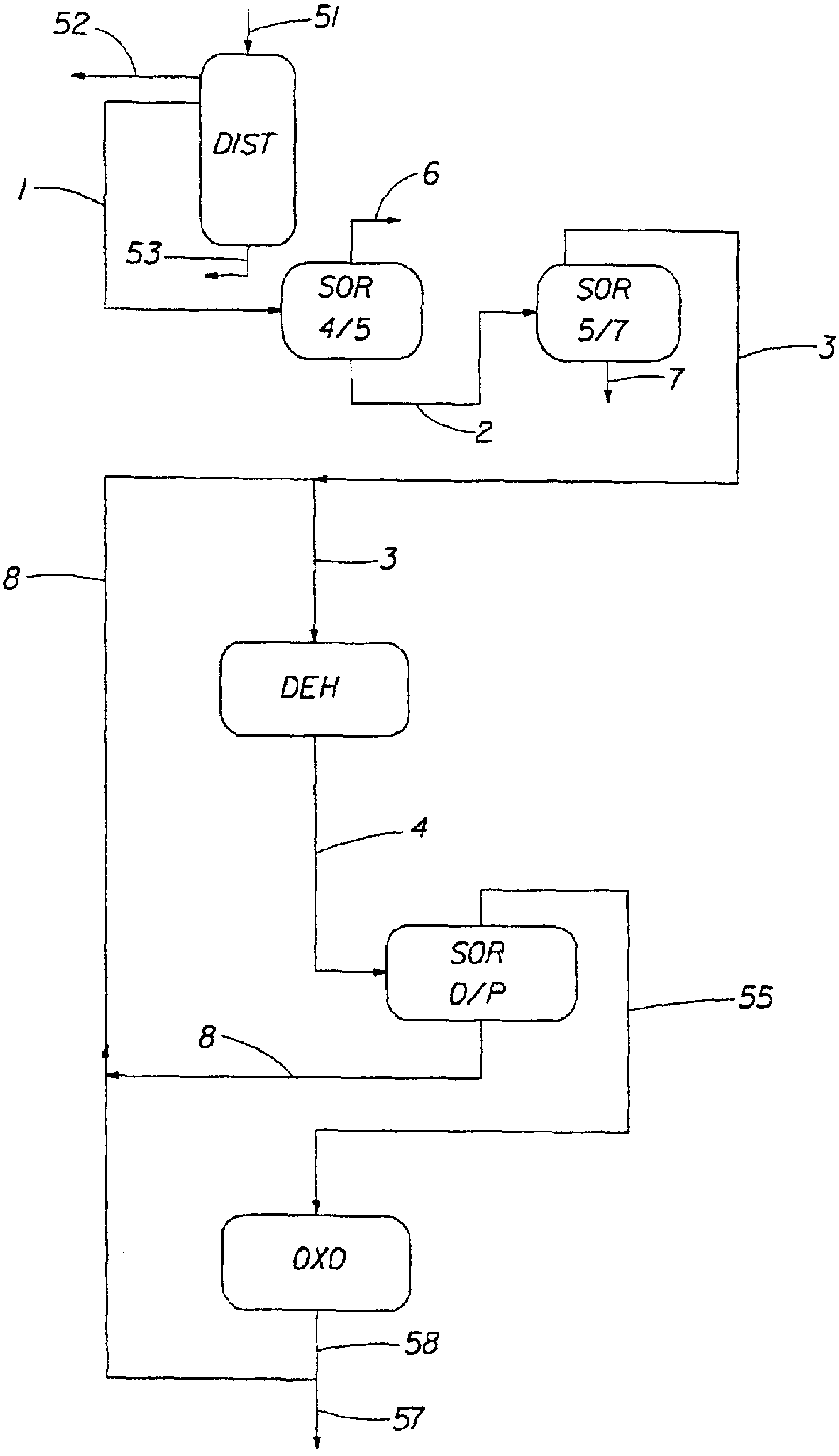
SURFACTANT-MAKING
e.g. ALKYLATION, SULFONATION

Fig. 8



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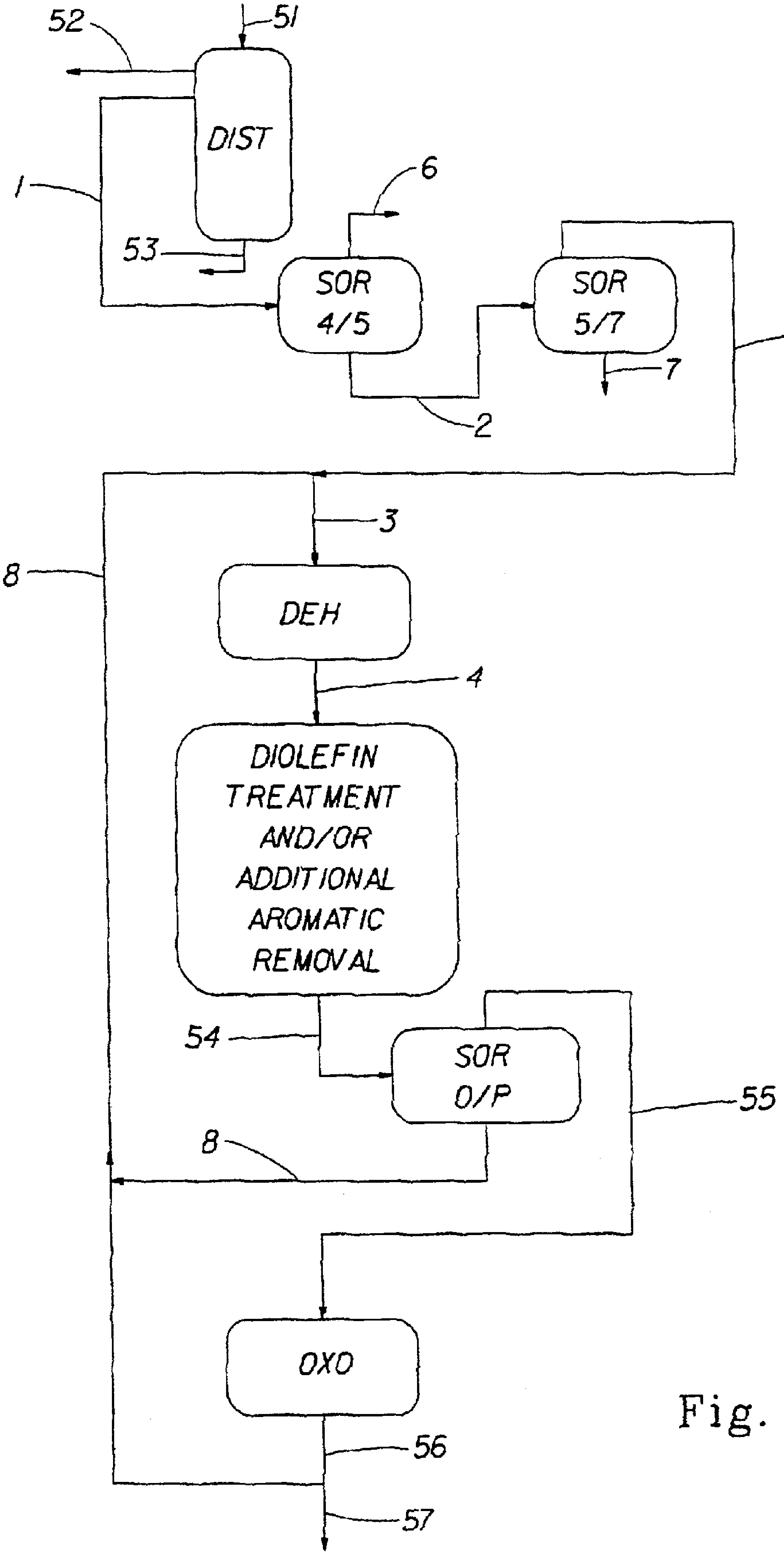
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DIOLEFIN TREATMENT AND/OR ADDITIONAL AROMATIC REMOVAL
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Fig. 10

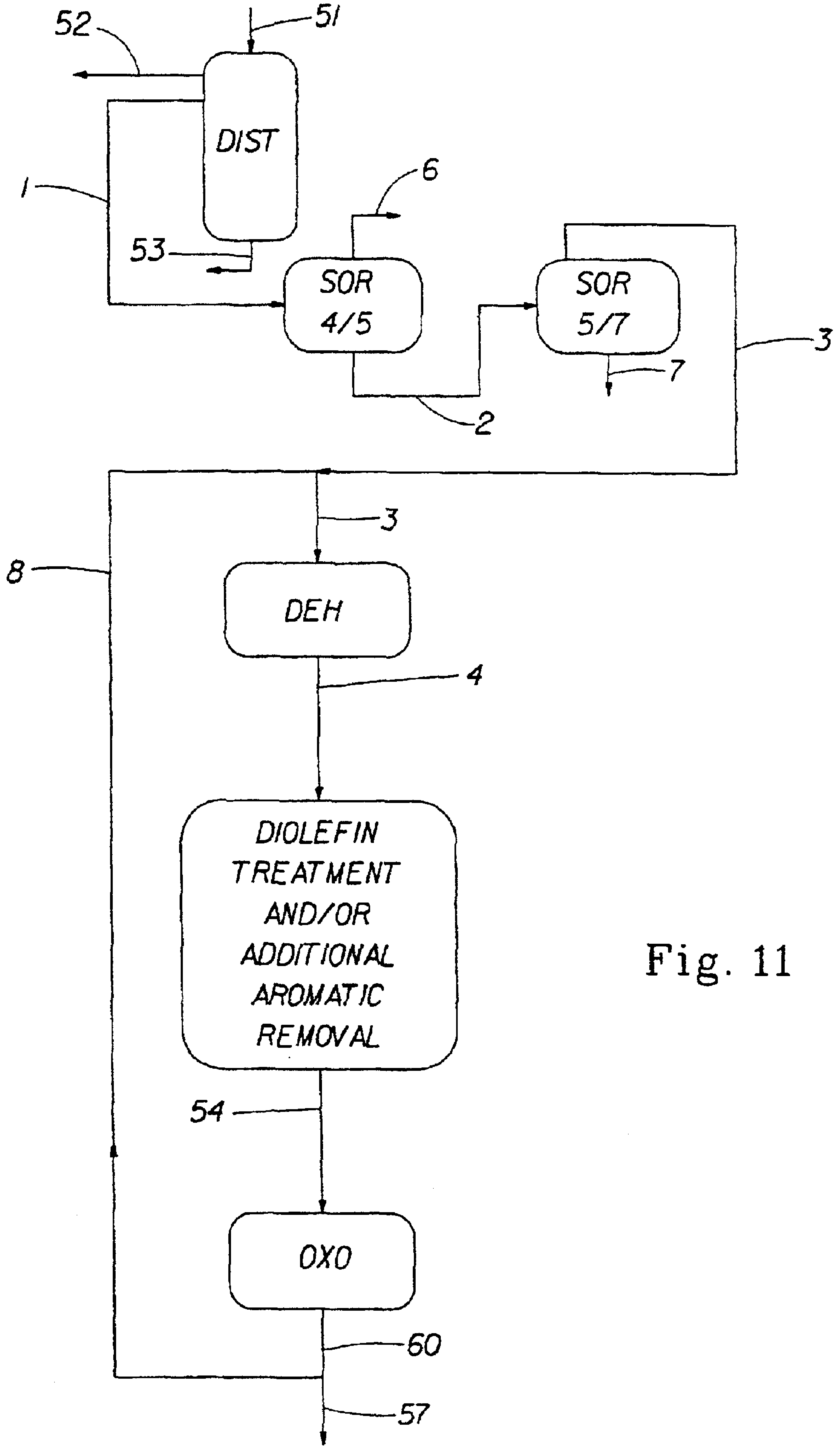
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Fig. 11

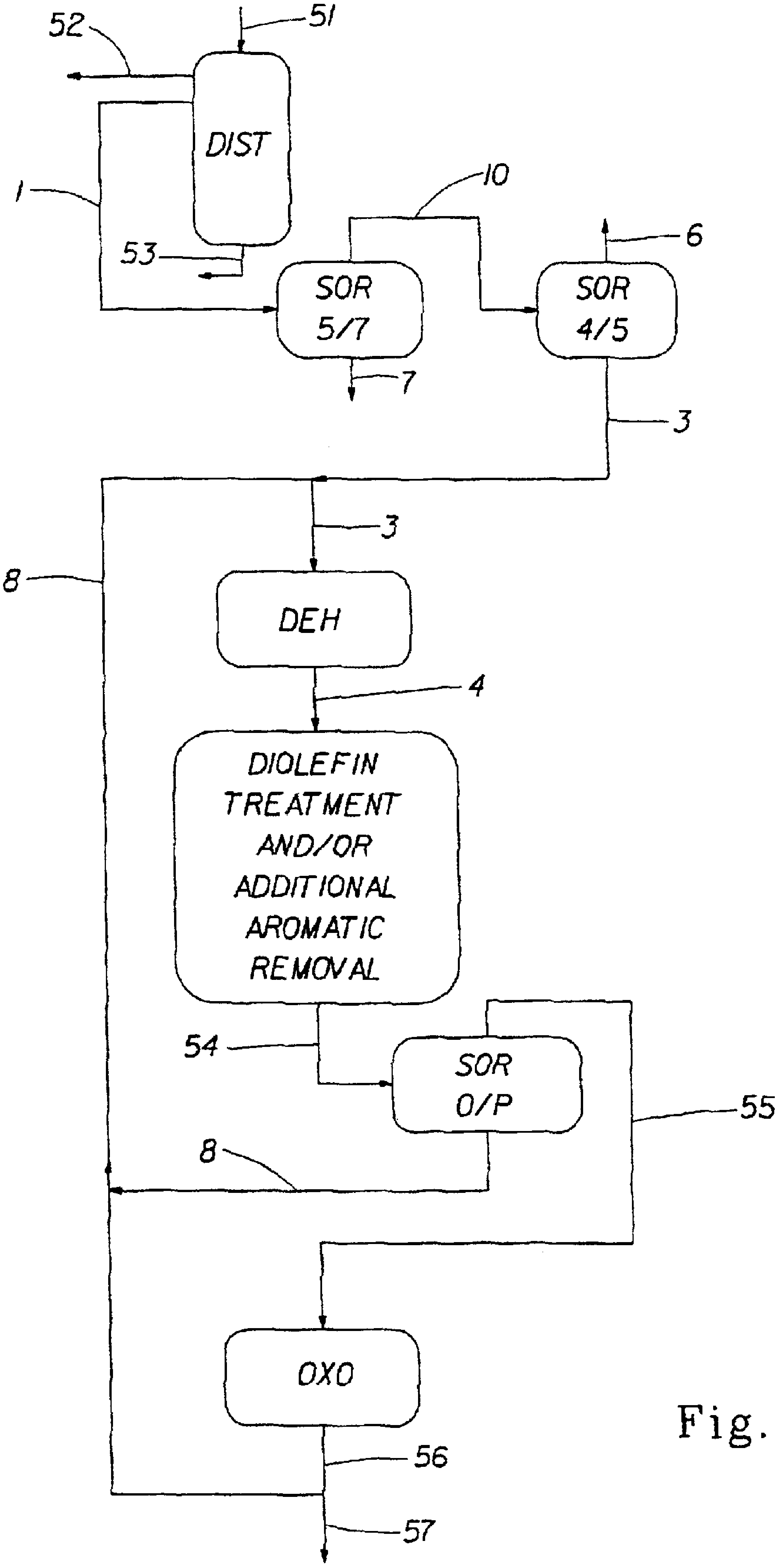
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Fig. 12

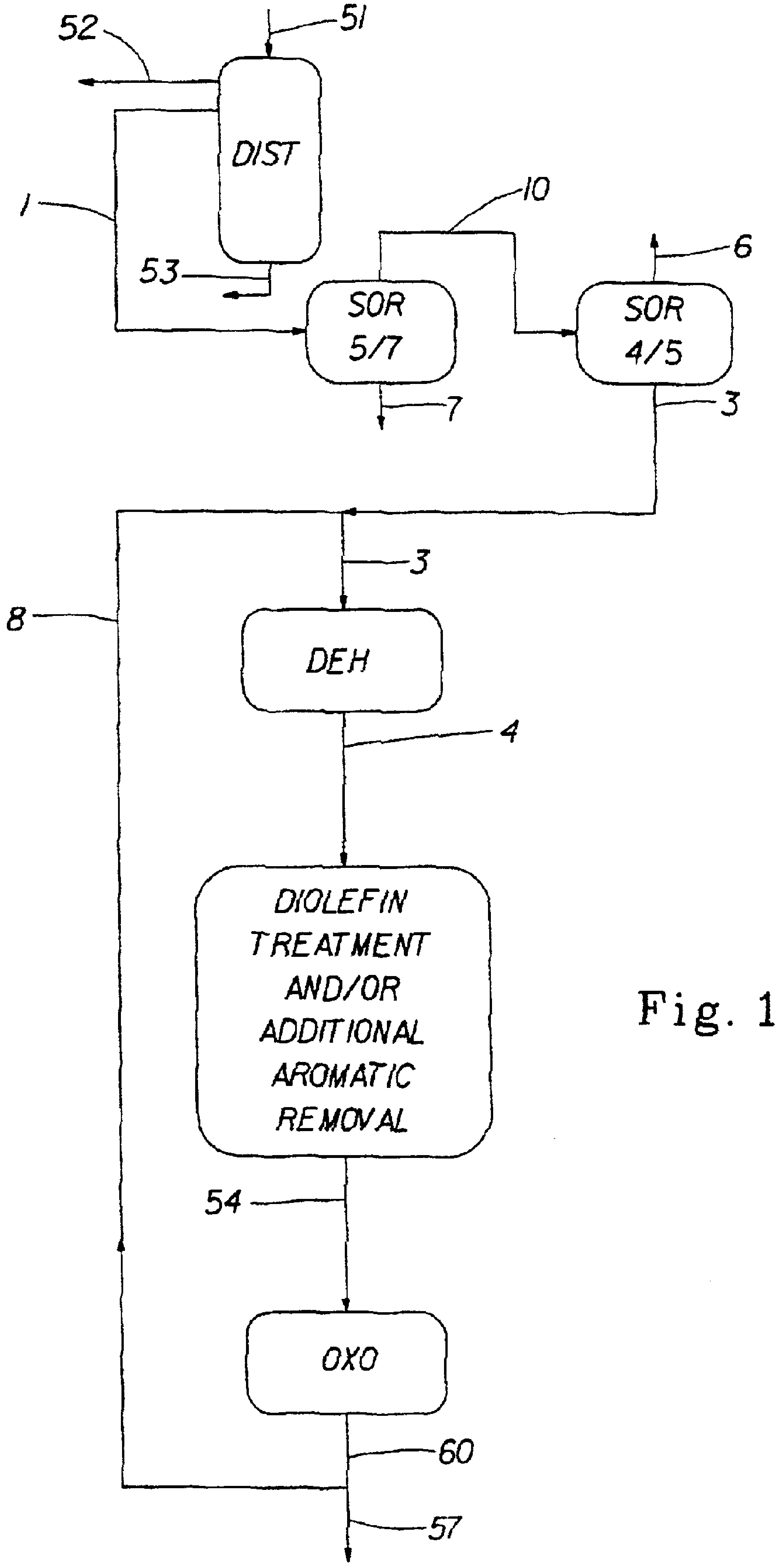
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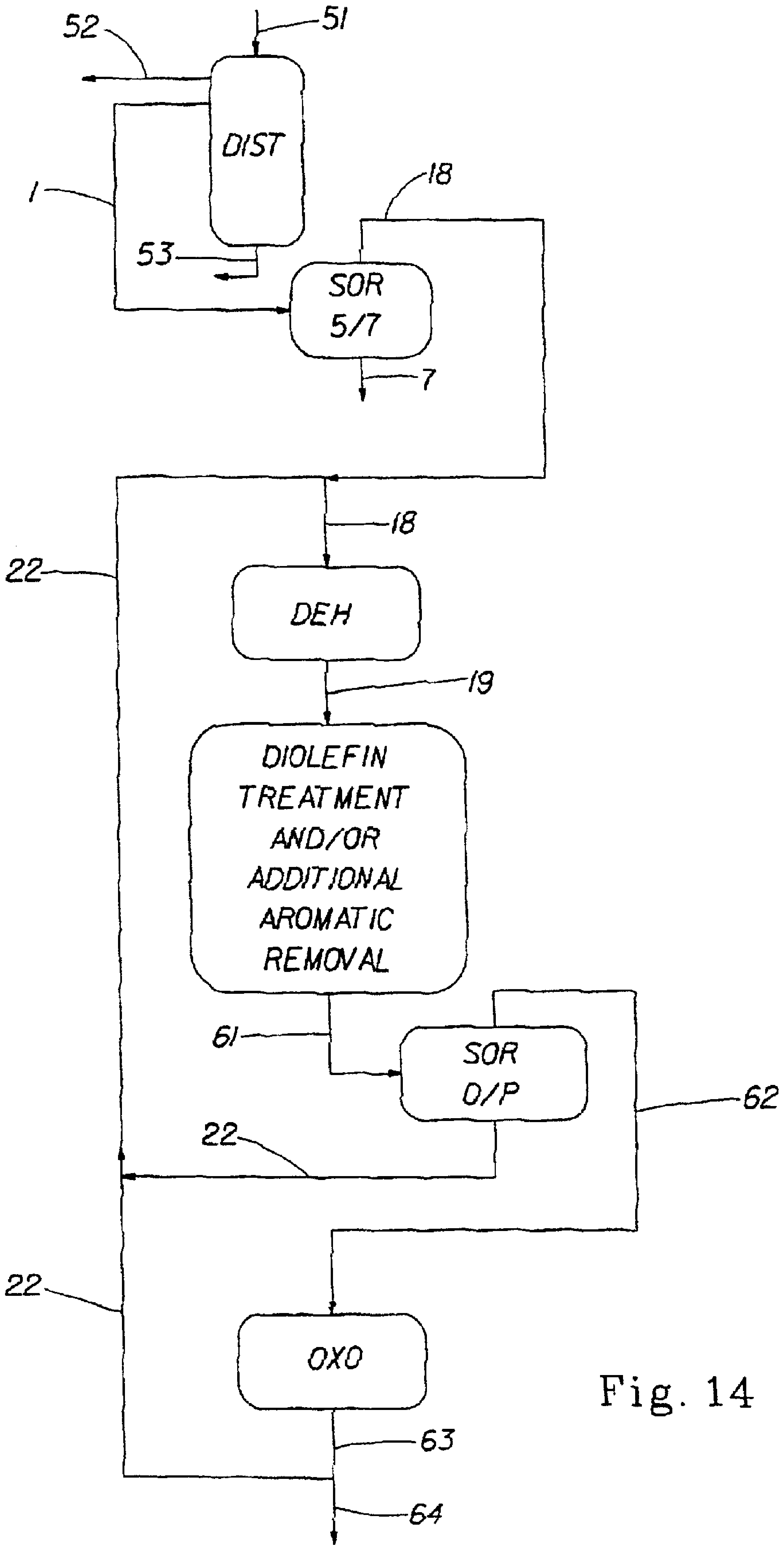
Fig. 13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OXO
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Fig. 14

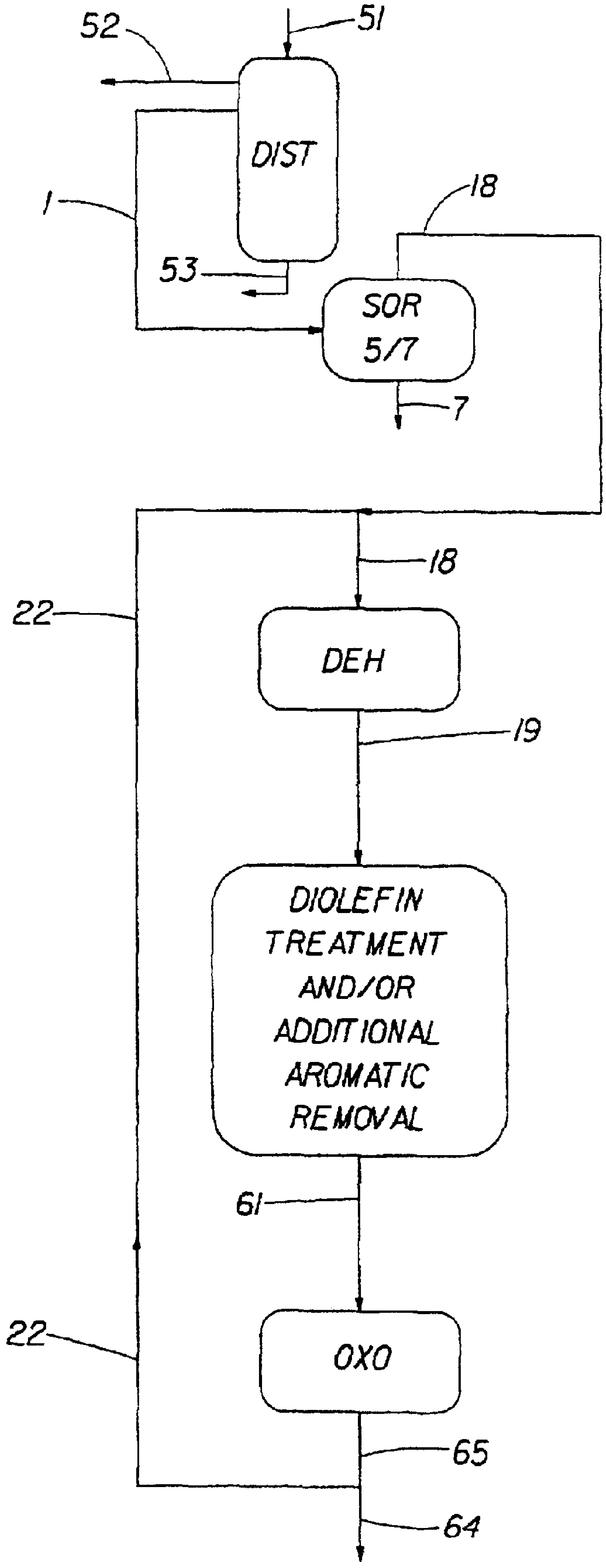
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Fig. 15

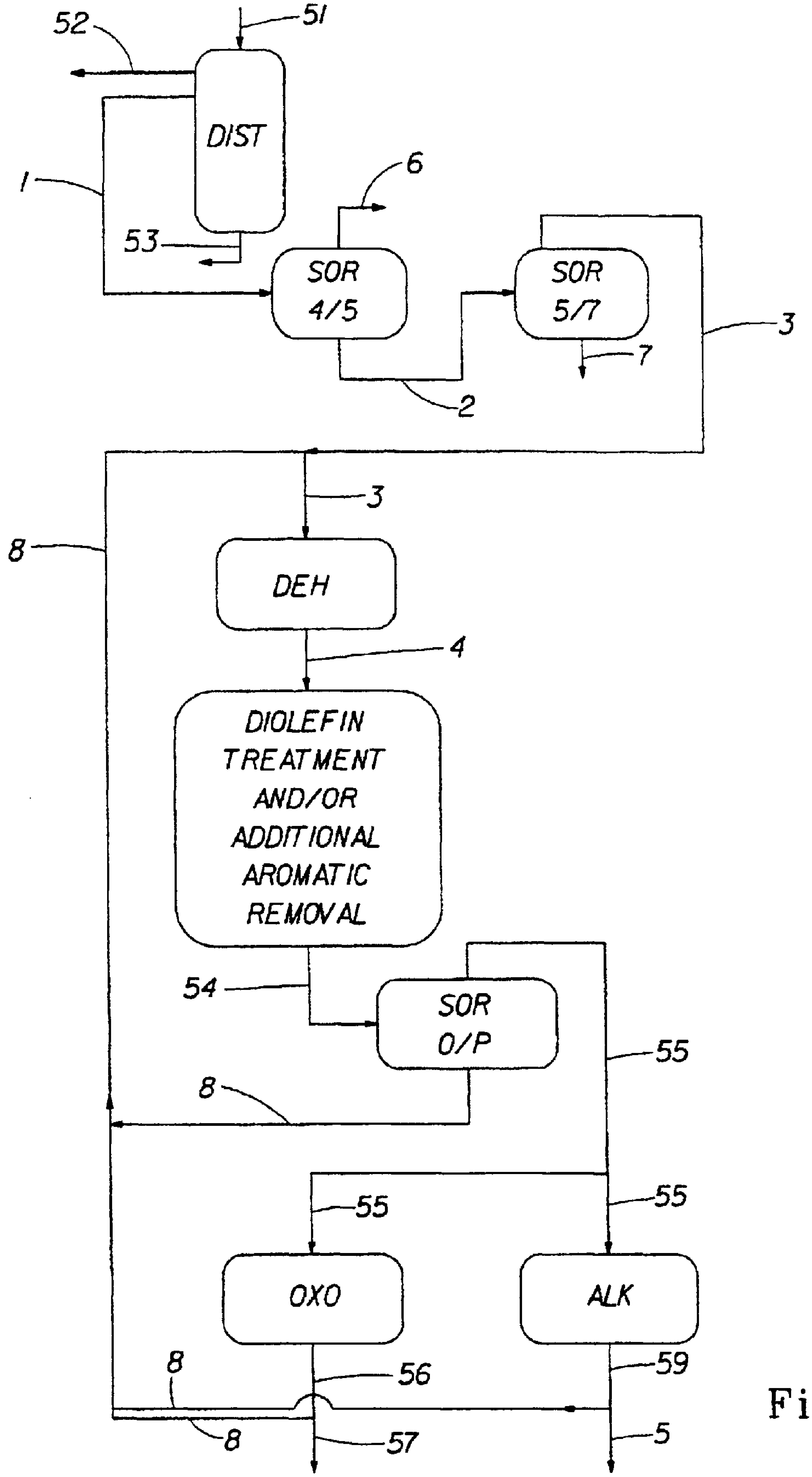
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Fig. 16

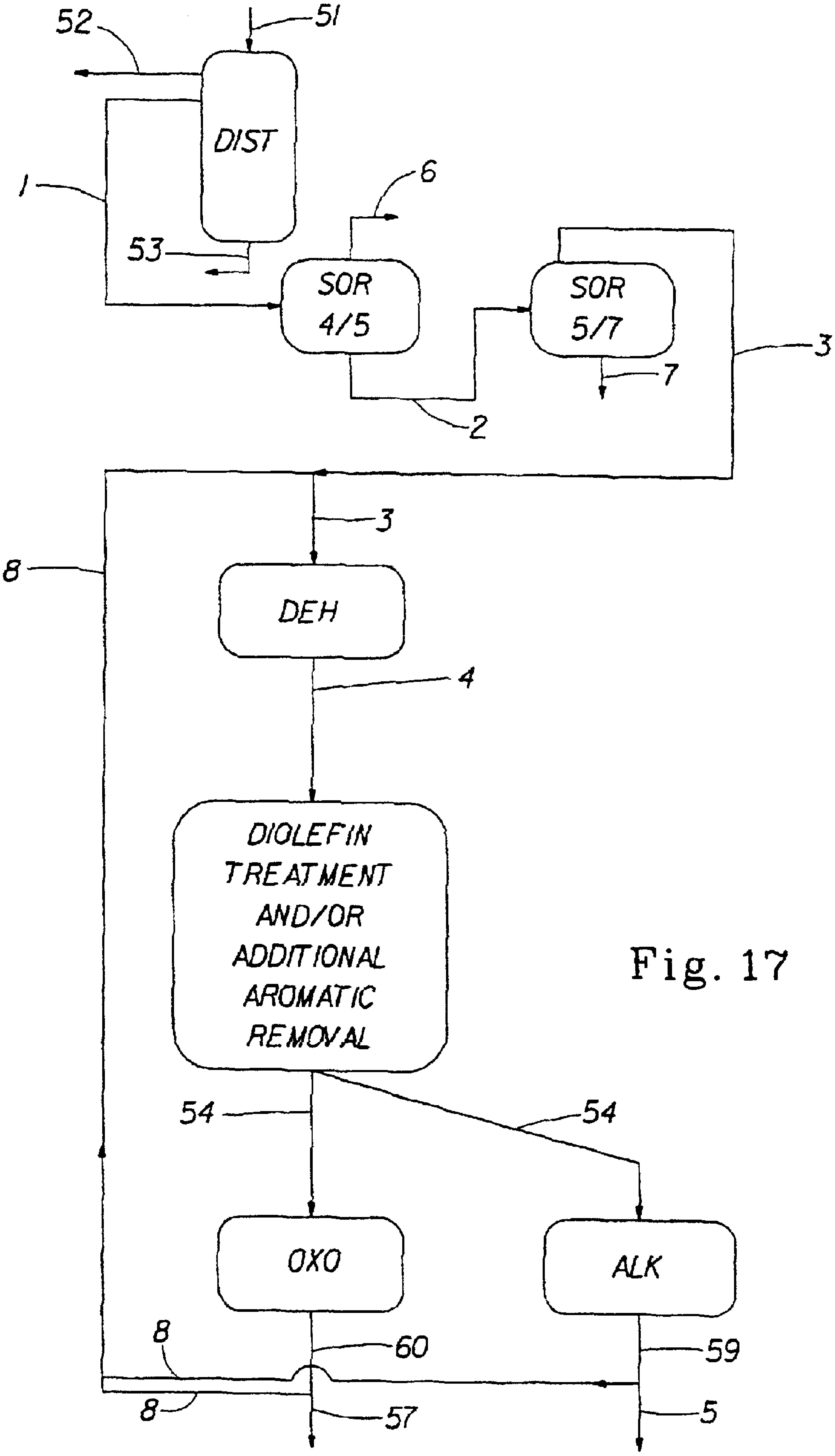
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Fig. 17

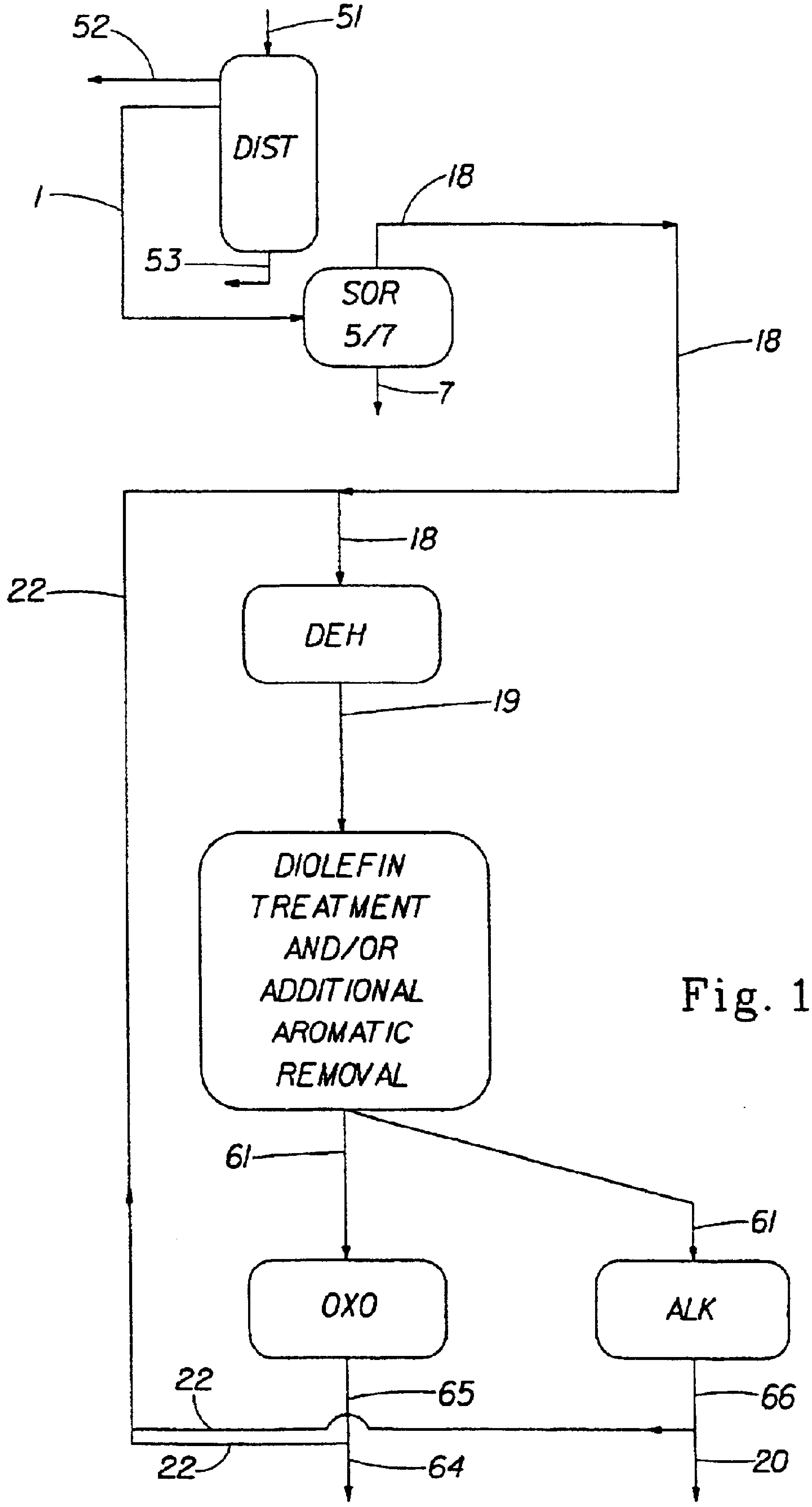
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Fig. 18

PROCESSES FOR MAKING SURFACTANTS VIA ADSORPTIVE SEPARATION AND PRODUCTS THEREOF

FIELD OF THE INVENTION

The present invention is in the field of processes for making surfactants useful in cleaning products. Preferred processes comprise particular combinations of adsorptive separation steps to separate certain hydrocarbons using specific means. Preferably these means include combinations of two or more particular adsorbent beds and two or more of particular types of rotary valves, as well as specified types of porous adsorbents having pore sizes in excess of those used in conventional linear alkylbenzene manufacture. Preferred processes further employ particular alkylation steps having specified internal isomer selectivities, or particular OXO reaction steps. The invention is also in the field of products of such processes, including certain modified alkylbenzenes, of modified alkylbenzenesulfonate surfactants, of detergent alcohols and surfactants derivable therefrom, and of consumer cleaning products, especially laundry detergents, containing them. Preferred processes herein employ unconventional sequences of adsorptive separation steps to secure certain branched hydrocarbon fractions which are then used in additional process steps as alkylating agents for arenes or for other useful surfactant-making purposes, such as OXO reactions to form particular detergent alcohols, followed by alkoxylation, sulfation or the like. Surprisingly, such fractions can even be derived from effluents from current linear alkylbenzene manufacture.

BACKGROUND OF THE INVENTION

Historically, highly branched alkylbenzenesulfonate surfactants, such as those based on tetrapropylene (known as “ABS” or “TPBS”) were used in detergents. However, these were found to be very poorly biodegradable. A long period followed of improving manufacturing processes for alkylbenzenesulfonates, making them as linear as practically possible (“LAS”). The overwhelming part of a large art of linear alkylbenzenesulfonate surfactant manufacture is directed to this objective. Large-scale commercial alkylbenzenesulfonate processes in use in the U.S. today are directed to linear alkylbenzenesulfonates. However, linear alkylbenzenesulfonates are not without limitations; for example, they would be more desirable if improved for hard water cleaning properties.

In the petroleum industry, various processes have recently been developed, for example for producing low viscosity lube oil or high-octane gasoline, which the inventors have now found provide useful new insight on how to delinearize hydrocarbons to a limited and controlled extent. Such deliberate delinearization, however, is not a feature of any current commercial processes in the different field of alkylbenzenesulfonate surfactant manufacture for consumer products. This is not surprising, in view of the overwhelming volume of LAS surfactant art teaching toward making linear compounds and away from delinearization.

The majority of commercial processes for making alkylbenzenes rely on H or aluminum chloride catalyzed alkylation of benzene. Quite recently, it has been discovered that certain zeolite catalysts can be used for alkylation of benzene with olefins. Such a process step has been described in the context of otherwise conventional processes for manufacture of linear alkylbenzenesulfonates. For example, the DETAL® process of UOP uses a zeolite alklylation catalyst. The DETAL® process and all other current commercial processes for alkylbenzenesulfonate manufacture are believed to fail to meet the internal isomer selectivity requirements of the preferred inventive process and alkylation catalyst defined hereinafter. Moreover, the DETAL® process catalyst or catalysts are believed to lack the moderate acidity and intermediate pore size of alkylation catalysts used in the preferred processes of the present invention. Other recent literature describes the use of mordenite as an alkylation catalyst, but no such disclosure makes the combination of specific process steps required by the instant invention. Moreover, in view of the linearity desired in alkylbenzenesulfonate products of conventionally known processes, they also generally include steps directed to the provision or making of a substantially linear hydrocarbon, not a delinearized one, prior to the alkylation. Possible exceptions are in U.S. Pat. No. 5,026,933 and U.S. Pat. No. 4,990,718. These and other known processes have numerous shortcomings from the standpoint of the detergent industry in terms of cost, catalyst limitations in the propylene oligomerization or olefin dimerization stage, presence of large volumes of distillation fractions that would need to be discarded or find non-detergent customers, and limited range of product compositions, including mixtures of chainlengths attainable. Such developments by the petroleum industry are, in short, not optimal from the standpoint of the expert formulator of detergent products.

It is also known in the art how to make linear alkylbenzenes using particular adsorptive separation processes. See U.S. Pat. No. 2,985,589. Such processes as described hitherto however do not provide branched alkylbenzenesulfonates.

It is also known in the art to prepare long-chained methyl paraffins for use as industrial solvents by processes which include urea clathration and separation on “molecular sieves”. See Chemical Abstracts, 83:100693 and JP 49046124 B4. This process assertedly involves double urea adduction, for example treating a petroleum fraction once with urea to remove n-alkanes as complexes, and then a second time with excess urea to obtain adducts of mixed n-alkanes and long-chained monomethyl paraffins. While this process may have some limited usefulness and may be included in the overall processes of the invention as most broadly defined, its limitations are considerable. This process, despite dating from 1974, is not known to have been incorporated into any overall process for making surfactants such as the modified alkylbenzenesulfonates described herein.

As further described in the Background Art section hereinafter, it is also known how to make various OXO alcohols and to make surfactants therefrom. However, the currently available OXO alcohols have shortcomings, such as in producing surfactants which are less soluble at a given chainlength than might be desired for the increasingly popular low wash temperatures or in relying on relatively expensive processes such as olefin oligomerization, isomerization and disproportionation; or in still having a relatively high content of linear material.

BACKGROUND ART

WO 97/39090, WO 97/39087, WO 97/39088, WO 97/39091, WO 98/23712, WO 97/38972, WO 97/39089, U.S. Pat. No. 2,985,589; Chemical Abstracts, 83:100693; JP 49046124 B4 Dec. 7, 1974; EP 803,561 A2 Oct. 29, 1997, EP 559,510 A Sep. 8, 1993; EP 559,510 B1 Jan. 24, 1996;

U.S. Pat. Nos. 5,026,933; 4,990,718; 4,301,316; 4,301,317; 4,855,527; 4,870,038; 2,477,382; EP 466,558, Jan. 15, 1992; EP 469,940, Feb. 5, 1992; FR 2,697,246, Apr. 29, 1994; SU 793,972, Jan. 7, 1981; U.S. Pat. Nos. 2,564,072; 3,196,174; 3,238,249; 3,355,484; 3,442,964; 3,492,364; 4,959,491; WO 88/07030, Sep. 25, 1990; U.S. Pat. Nos. 4,962,256, 5,196,624; 5,196,625; EP 364,012 B, Feb. 15, 1990; U.S. Pat. Nos. 3,312,745; 3,341,614; 3,442,965; 3,674,885; 4,447,664; 4,533,651; 4,587,374; 4,996,386; 5,210,060; 5,510,306, WO 95/17961, Aug. 16, 1995; WO 95/18084; U.S. Pat. Nos. 5,510,306; 5,087,788; 4,301,316, 4,301,317; 4,855,527; 4,870,038; 5,026,933; 5,625,105 and U.S. Pat. No. 4,973,788 are useful by way of background to the invention. Cited documents EP 559,510 A and B in particular relate to making high-octane gasolines by recycling streams to an isomerization reactor. Grafted porous materials of EP 559,510 and grafting of zeolites, e.g., by tin alkyls, are useful in the present invention. U.S. Pat. No. 5,107,052 likewise relates to improving octane ratings of gasoline and describes separating C4–C6 methyl paraffins using various molecular sieves such as AlPO4–5, SSZ-24, MgAPO-5 and/or MAPSO-5 containing less than 2% water. These sieves are assertedly capable of selectively adsorbing dimethyl paraffins and not adsorbing monomethyl and normal paraffins.

The manufacture of alkylbenzenesulfonate surfactants has recently been reviewed. 5 See Vol. 56 in "Surfactant Science" series, Marcel Dekker, New York, 1996, including in particular Chapter 2 entitled "Alkylarylsulfonates: History, Manufacture, Analysis and Environmental Properties", pages 39–108 which includes 297 literature references. This work provides access to a great deal of literature describing various processes and process steps such as dehydrogenation, alkylation, alkylbenzene distillation and the like. See also 10 "Detergent Alkylate" in Encyclopedia of Chemical Processing and Design, Eds. Mc.Ketta and Cunningham, Marcel Dekker, N.Y., 1982., especially pages 266–284. Adsorption processes such as UOP's Sorbex process and other associated processes are also described in Kirk Othmer's Encyclopedia of Chemical Technology, 4th Edition, Vol. 1, see "Adsorption and Liquid Separation", including pages 583–598 and references cited therein. See also publications by UOP Corp., including the "Processing Guide" available from UOP Corp., Des Plaines, Ill. Commercial paraffin isolation and separation processes using molecular sieves include MOLEX® (UOP Inc.), a liquid-phase process, and ISOSIV® (Union Carbide Corp.) as well as ENSORB® (Exxon Corp.) and TSF® or Texaco Selective Finishing process, which are vapor-phase processes. All these processes are believed to use 5 Angstrom molecular sieves as porous media. Where not noted herein, the operating temperatures, pressures and other operating conditions and apparatus for any process step are conventional, that is, as already well known and defined in the context of manufacturing linear alkylbenzenesulfonate surfactants. Documents referenced herein are incorporated in their entirety.

U.S. Pat. No. 3,732,325 issued May 8, 1973 describes a process for sorptive separation of aromatic hydrocarbons.

U.S. Pat. No. 3,455,815 issued Jul. 15, 1969, U.S. Pat. No. 3,291,726 issued Dec. 13, 1966, U.S. Pat. No. 3,201,491 issued Aug. 17, 1965 and U.S. Pat. No. 2,985,589 issued May 23, 1961 describe simulated moving bed sorptive separation processes for hydrocarbons.

U.S. Pat. No. 5,780,694 issued Jul. 14, 1998 and WO 98/23566 published Jun. 4, 1998 incorporated herein by reference relate to certain branched detergent alcohols and to surfactants derivable therefrom. These documents include a description of the well-known OXO process and of catalysts suitable for hydroformylation See especially '694 columns 10 and 11.

U.S. Pat. No. 5,510,564 issued Apr. 23, 1996 incorporated herein by reference describes processes for purifying hydrocarbons, especially in the context of aromatics removal.

U.S. Pat. No. 5,276,231 issued Jan. 4, 1994 describes aromatics removal from hydrocarbons by means of sulfolane extraction.

U.S. Pat. No. 4,184,943 issued Jan. 22, 1980 describes sorptive hydrocarbon separations.

U.S. Pat. No. 4,006,197 issued Feb. 1, 1977 describes sorptive hydrocarbon separations of n-paraffins.

U.S. Pat. No. 5,220,099 issued Jun. 15, 1993 and U.S. Pat. No. 5,171,923 issued Dec. 15, 1992 describe purifying paraffins by removal of aromatics, sulfur, nitrogen and oxygen containing compounds, and color bodies by magnesium Y or Na-X zeolite sorption.

Surfactant Science Series, Volume 7, "Anionic Surfactants", Part 1, Marcel Dekker, N.Y., Ed. W. Linficld, 1976, Chapter 2 "Petroleum-Based Raw Materials for Anionic Surfactants", pages 11–96 provides general background including for the OXO process (see pp 71 and following) and for certain feedstocks (see p 60 and following). To be noted, this reference under the heading "branched-chain olefins" at page 65 and following does not describe branched-chain olefins suitable for use in the instant process—the identified "branched-chain" olefins being unsuitable biologically "hard" types. The OXO process discussion at pp. 72 and following shows conversion of linear olefin to mixtures of"branched" and linear aldehydes and/or alcohols. Again, this usage of the term "branched" differs from the present invention—processes herein all involve use of at least partially mid-chain methyl-branched feedstocks as the principal source of branching, the OXO reactions herein providing specific methyl-branched primary alcohols wherein only secondary aspects of any branching are due to OXO reaction.

Separately, the reference immediately supra and references cited therein also describe the UOP OLEX® process and sorbents useful therein, see for example pages 60–63 making reference to Cu- or Ag-doped zeolites. See more particularly U.S. Pat. No. 3,969,276 issued Jul. 13, 1976 for X- or Y-type zeolites doped with silver. See also D. B. Broughton and R. C. Berg, Hydrocarbon Process, Vol. 48(6), 115 (1969); D. B. Broughton and R. C. Berg, National Petroleum Refiners Association, 1969 Annual Meeting, Mar. 23, 1969, technical paper AM-69-38; D. B. Broughton and R. C. Berg, Chemical Engineering, Jan. 26, 1970, page 86, article entitled "Two processes team up to make linear monoolefins".

Kirk Othmer's Encyclopedia of Chemical Technology, 4th Edition, Vol. 1, pages 893–913 (1991), article entitled "Alcohols, Higher Aliphatic", sub-heading "Synthetic Processes" describes an OXO reaction to form detergent alcohols, see especially "Modified Cobalt Catalyst, One-Step, Low Pressure Process", at pages 904–906. Note once again that the diagrams showing methyl-branched alcohols, see for example page 904, are exclusively made from linear precursors and the OXO-branching is in the 2-position (as in the above-identified reference).

See also Surfactant Science Series, Volume 56, "Anionic Surfactants", Marcel Dekker, N.Y., Ed. W. Linfield, 1996, Chapter 1 "Raw Materials for Aniionic Surfactant Synthesis", pages 1–142 incorporated by reference, for additional description of feedstocks common in detergent manufacture, for description of known processes for sorptive and other separations, for descriptions of detergent alkylation, and for description of OXO or hydroformylation process steps (see for example pp. 23–25).

OXO process literature includes also "New Syntheses with Carbon Monoxide", Ed. J. Falbe, Springer-Verlag, New York, 1980.

Commercial practice for making detergent alcohols which differ from those accessible herein is currently understood to include the sequence: isolation of linear paraffins from kerosene by sorptive separation, dehydrogenation by the PACOL® process (or similar) to linear internal olefins, isolation of the olefin from paraffin by the OLEX® process (or similar), and OXO reaction in one of two ways, either by a conventional OXO catalyst to give a 2-alkyl substituted primary alcohol, e.g., as in ENI's LIAL® alcohols, or by isomerization of the olefin to the terminal position followed by terminal OXO addition, as practiced by the Shell/Mitsubishi process.

See also WO97/01521 A1 published Jan. 16, 1997 and 95 ZA-0005405 published Jun. 25, 1995. See also various technical bulletins and publications of Sasol and/or Sastech of South Africa, especially in relation to already known or available OXO alcohols made or makable by the OXO processes proprietary to these companies.

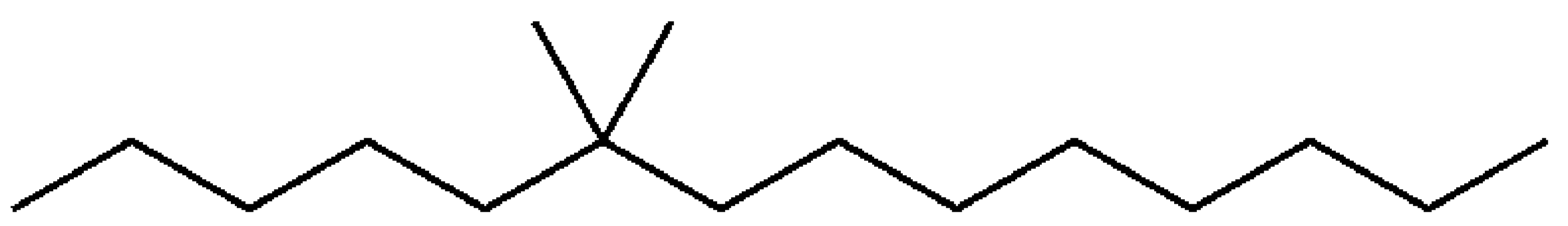
BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. **1**–**18** are schematic drawings of some processes in accordance with the invention. FIG. **8** shows in more detail a configuration of two adsorptive separation units, each individually being of a type as found in the first two adsorptive separation steps of FIG. **1** and FIG. **2**. Note that the FIG. **8** interconnections are as shown in FIG. **1**., but differ from those shown in FIG. **2**.

Solid lines are used for essential process steps and process streams. Dashed lines identify steps and streams which may not be essential in the processes as most broadly defined but which are present in various preferred process embodiments. Rounded rectangles identify process steps, stages or units. Numbered lines identify feedstocks, intermediate process streams and products. "SOR" identifies an adsorptive separation step. "4/5" identifies that the adsorptive separation uses small-pore zeolite, especially Ca zeolite 5A, which is completely conventional in linear alkylbenzene manufacture. "5/7" identifies that the adsorptive separation uses a porous material such as SAPO-11 or any equivalent porous material having the ability to adsorb

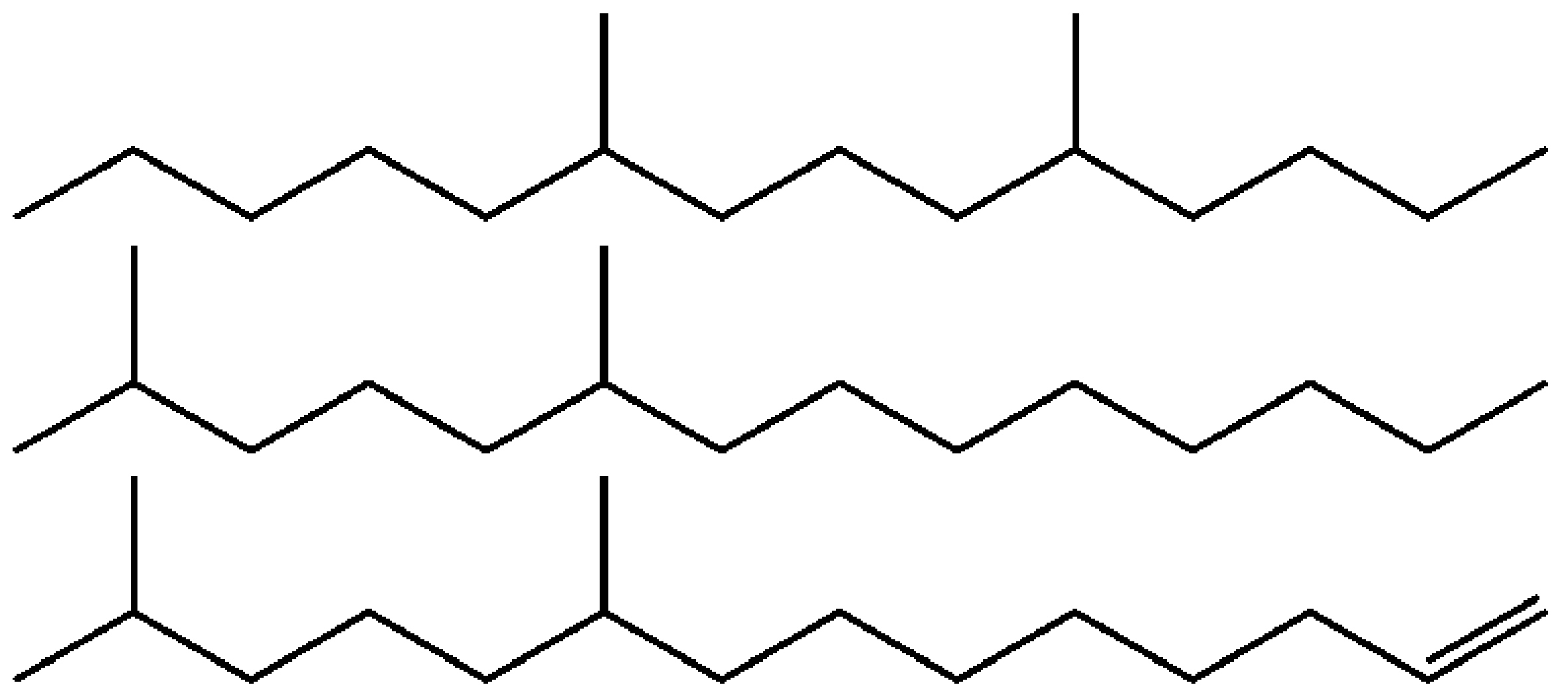
monomethyl branched paraffins and/or
monomethyl branched monoolefins and/or
nongeminal dimethyl paraffins and/or
nongeminal dimethyl olefins

while rejecting geminal dimethyl hydrocarbons, cyclic (five-, six- or higher membered ring) hydrocarbons or higher branched hydrocarbons, whether aromatic or aliphatic. The term "geminal dimethyl" as used herein means that there are two methyls attached to an internal carbon atom of a hydrocarbon, as in

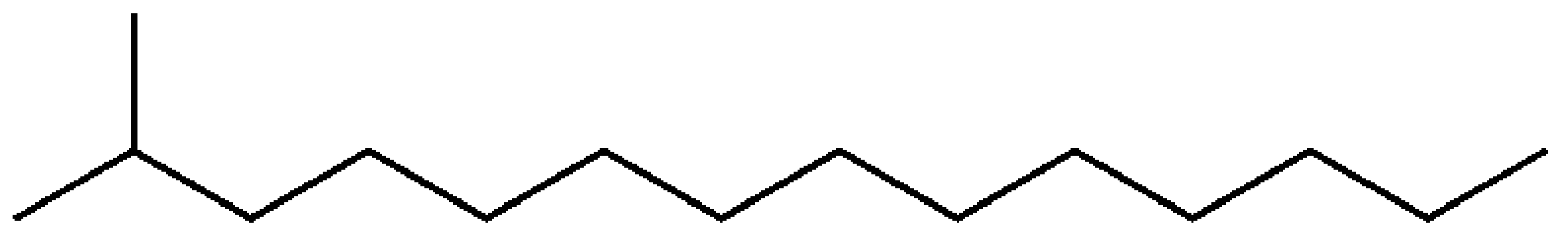


Only sorptive stage SOR 4/5 and/or sorptive stage SOR 5/7 herein are of the type used in stage (a) of modified alkylbenzene manufacture or stage (A) of modified primary OXO alcohol manufacture as described hereinafter.

The large-pore porous materials herein should not adsorb such hydrocarbons. In contrast, the following hydrocarbons should be adsorbed. They are illustrative of what is meant by the term "nongeminal dimethyl" hydrocarbons:



Note that any methyl moieties at the ends of the main chain are not counted in defining the term "nongeminal dimethyl" as used herein. Further, consistent with this convention, the following hydrocarbon should be adsorbed by the large-pore porous material. It is a "monomethyl" hydrocarbon:



Large-pore porous materials suitable for use herein are more filly and more generally described in the specification hereinafter. "DEH" identifies a step of at least partial dehydrogenation of a stream (partial dehydrogenation being typical in conventional linear alkylbenzene manufacture though complete dehydrogenation can also be used herein), and "ALK" identifies an alkylation step. Any step, stage or unit identified by a rounded rectangle can in practice comprise only the essential step or can, more typically, include within it an additional step or steps which may be optional in the invention as most broadly defined, or which may be essential only in a preferred embodiment. Such additional steps not shown include, for example, distillation steps of types commonly practiced in the art.

In FIGS. **9**–**18**, "DIST" where present identifies a distillation step, "SOR O/P P" where present identifies a sorptive olefin/paraffin separation step, for example OLEX® process of UOP as used in stage (C) of modified primary OXO alcohol manufacture described in detail hereinafter and "OXO" where present identifies a hydroformylation process step. Such process steps are well-known in the art: see the "Background Art" section.

With the aforementioned conventions in mind, it will be seen that FIG. **1** illustrates a process having, in sequence, two adsorptive separations, collectively in accordance with adsorptive separation stage (a) of the invention as defined hereinafter; followed by a dehydrogenation step (step (b) hereinafter); optionally followed by an alkylation step (step (c) hereinafter). While step (c) is optional in the invention as most broadly defined, it is present in all preferred embodiments which relate to making modified alkylbenzenes in accordance with the invention and, when making modified alkylbenzenesulfonate surfactants, is typically followed by (d) sulfonation, (e) neutralization and (f) mixing to formulate into a consumer cleaning product. Steps (d) though (f) use conventional means and are not explicitly shown in FIGS. **1**–**8**.

In the FIG. **1** process, a hydrocarbon feed **1** passes to the first adsorptive separation step, for example a step in conformity with U.S. Pat. No. 2,985,589, which uses a bed of 4–5 Angstrom zeolite. A linear hydrocarbon stream is discarded as a reject stream **6**. For comparison, in conventional linear alkylbenzene manufacture, stream **6**, comprising a high proportion of linear hydrocarbons, would pass to DEH while step SOR 5/7 and associated streams would be absent. In the present process according to FIG. **1**, an intermediate branched-enriched hydrocarbon stream is retained **2** and passes to a second adsorptive separation. The second adsorptive separation uses a particular type of porous media and produces a branched-enriched stream **3** (product of stage (a) as defined hereinafter) which passes to the dehydrogenation reactor (DEH); as well as a reject stream **7**. The particular type of porous media is preferably a "large-pore" zeolite, such zeolite herein being characterized by a pore size larger than that of the zeolites used in making linear alkylbenzenes, and very preferably, a pore size of from above about 5 Angstrom to about 7 Angstrom though larger pore materials can be used and their pore sizes can be "tuned down", for example by use of tin alkyls. Stream **4** represents dehydrogenated branched-enriched hydrocarbon, stream **8** represents recycled branched paraffins. Also shown is an alkylation step according to the invention which is included in a preferred embodiment of the invention. Output from the alkylation step is a modified alkylbenzene as defined elsewhere herein.

FIG. **2** is a schematic drawing identifying steps in another embodiment of the present process. While generally similar to the process of FIG. **1**, the FIG. **2** process has important differences, especially in that the adsorptive separation steps are reversed with respect to pore sizes in the adsorbent beds.

FIG. **4** is a schematic drawing identifying an embodiment of the invention which starts with a hydrocarbon feedstock **23** such as branched effluent from a conventional linear alkylbenzene manufacturing process, or from a conventional linear detergent alcohol process. An adsorptive separation step using particular porous media is used to produce a reject stream **27** and a branched-enriched stream **24**. The latter is dehydrogenated in the step marked DEH. The particular type of porous media is preferably a zeolite having pore size larger than that of the zeolites used in making linear alkylbenzenes, and very preferably has pore size of from above about 5 Angstrom to about 7 Angstrom. The dehydrogenated hydrocarbon stream **25** passes to an alkylation step ALK from which passes a modified alkylbenzene product **26**. A optional recycle stream is identified as **28**.

FIG. **3** is a schematic drawing identifying an embodiment of the invention similar to that of FIG. **4** but using substantially different feedstock and intermediate process stream compositions. For example, FIG. **3** can utilize as feed **17** a C10–C14 paraffin fraction having the intrinsic linear/branched paraffin ratio as received, and from which cyclics, aromatics, gem-dimethyl, ethyl- or higher-than-ethyl branched hydrocarbons are removed as part of the present process.

When comparing FIG. **3** and FIG. **4** it may appear in view of the apparently identical configuration of steps that the processes illustrated therein are identical. This is not the case in view of the very different results achieved in consequence of changing the hydrocarbon feed. FIG. **4** uses as hydrocarbon feed **23** an effluent stream from a linear alkylbenzene manufacturing facility and produces a modified alkylbenzene **26** which is predominantly branched. The FIG. **4** process could be built as an "add-on" to a standard linear alkylbenzene manufacturing plant. In contrast, FIG. **3** uses as hydrocarbon feed a mixture of linear and branched paraffins of the kind intrinsically present in, say, a jet/diesel cut derived from kerosene which has not been processed in a linear alkylbenzene manufacturing facility. The FIG. **3** process produces a modified alkylbenzene which contains a mixture of methyl-branched (unconventional, in accordance with the invention) and linear (conventional) alkylbenzenes. The FIG. **3** process can be built as a "stand-alone" facility requiring no connection to a conventional linear alkylbenzene manufacturing facility. These observations are intended to better illustrate the present process and should not be taken as limiting.

FIG. **5**, FIG. **6** and FIG. **7** are schematic drawings identifying additional embodiments of the invention to accommodate other different hydrocarbon feeds. More specifically, these Figures illustrate processes which accommodate mixed paraffin/olefin feeds.

FIG. **8** shows in more detail the particular configuration of adsorptive separations which is found in other process illustrations, e.g., in FIG. **1** and FIG. **6**. Each block represents an adsorptive separation unit. Within each block, a vertical array of adsorptive separation beds (AC in the left of each block) is controlled by a rotary valve (RV). The adsorptive separation is accompanied by distillations in columns RC and EC. The streams marked "Feed", "Extract" and "Raffinate" of the leftmost adsorptive separation mcorrespond with the streams marked "**1**", "**6**" and "**2**" in FIG. **1**. The raffinate stream of the first adsorptive separation (and not the extract as would be the case in conventional linear alkylbenzene manufacture) becomes the feed for the second adsorptive separation. The raffinate of the second adsorptive separation in FIG. **8** corresponds with stream **7** in FIG. **1**. The extract of the second adsorptive separation in FIG. **8** corresponds with stream **3** in FIG. **1**: this is the stream which in the present process is dehydrogenated and/or alkylated.

FIG. **8**, as noted, also serves to illustrate in more detail individual adsorptive separations herein. Thus, while the connections are not as shown in FIGS. **2**, **3**, **4**, **5** and **7**, any single adsorptive separation of FIGS. **2**, **3**, **4**, **5** and **7** can be represented in more detail using an appropriate interconnection of the detailed units illustrated in either block of FIG. **8**.

The convention is used in FIGS. **1**–**7** to depict hydrocarbon fractions adsorbed by the porous media as exiting above the adsorptive separations marked "SOR" while fractions not adsorbed are shown as exiting below the adsorptive separations marked "SOR". The fraction exiting "above" is sometimes in the art referred to as an "adsorbate" or "extract" and the fraction exiting "below" is sometimes referred to as a "raffinate" or "effluent". The "above" and "below" conventions used here are intended to make reading the process Figures more convenient and should not be taken as limiting the practical executions of the present process to any particular geometrical arrangement.

Using principles similar to those used in FIGS. **1**–**8**, FIG. **9** illustrates a process for the production of modified primary OXO alcohols using mid-chain methyl- branched internal olefins having carbon numbers suitable for detergent application as intermediates and in which the OXO catalyst largely pre-isomerizes the internal olefin to an alpha-olefin and then hydroformylates predominantly at the terminal carbon atom. In more detail, crude hydrocarbon feed **51** is distilled using distillation column DIST to secure a hydrocarbon feed suitable for the remainder of the process. Feed **1** can desirably be a narrow-carbon range paraffin cut. A light distillation cut **52** and a heavy distillation cut **53** are also obtained but not further used for making the instant OXO alcohols. Hydrocarbon feed **1** is passed through a simulated moving bed sorptive separation system comprising units SOR 4/5 followed by SOR 5/7, each suitably of MOLEX® type, connected in the order shown. The configuration is set such that a linear-enriched stream (an adsorbate) rich in linear paraffin and identified as **6** in FIG. **9** is rejected from unit SOR 4/5. An intermediate branched-enriched stream (a raffinate) **2**, which is enriched in methyl-branched paraffins, proceeds to unit SOR 5/7. Reject stream **7** from SOR 5/7 which contains unwanted cyclics, aromatics, ethyl-branched and higher-branched paraffins is discarded. Branched-enriched stream **3** from SOR 5/7 now a purified methyl-branched paraffin stream, proceeds to dehydrogenator DEH, for example of PACOL® type where up to 20% of it is converted predominantly to the corresponding mono-olefins. Branched-enriched stream (olefinic) **4**, containing said mono-olefins together with unreacted paraffins and some diolefin impurity, proceeds to SOR O/P, which is a simulated moving-bed adsorptive separation system configured to use OLEX® or similar approaches for the separation of olefins from paraffins. Suitably, for example, the adsorbent is copper or silver on zeolites X or Y. From SOR O/P, a purified olefinic branched-enriched stream (the adsorbate) **55**, now mostly methyl-branched olefins, proceeds to an OXO reactor. Recycle stream **8** is predominantly methyl-branched paraffins. The OXO reactor is configured for what is termed in the art as a "one-step low-pressure OXO process" using a catalytic metal other than iron, said metal being modified with bulky phosphine ligands (see the references in Background). Crude modified primary OXO alcohol, product stream **58**, is separated from recyclable material using distillation and other ancilliary means not shown and the clean modified primary OXO alcohol, now freed from recyclable material, emerges as stream **57**. See the table hereinafter for more detailed description of the composition of each stream.

FIG. **10** is similar to FIG. **9** with the exception that it incorporates one or more treatment steps after the dehydrogenation step, to hydrogenate diolefin impurity produced in the dehydrogenator and convert it back to mono-olefin. This is typically a DEFINE® type stage licensable from UOP Corp. Additionally present can be one or more additional aromatic removal steps, for example the PEP® process of UOP, principally to remove aromatic impurities formed during the dehydrogenation.

FIG. **11** is similar to FIG. **10** except that it is simplified in that it uses an olelin/paraffin mixture as feed to the OXO reactor and in that recycle stream **8** is now a large fraction (>70%) of the OXO reactor output.

FIG. **12** is similar to FIG. **10** except that units SOR 4/5 and SOR 5/7 have a reverse configuration.

FIG. **13** is similar to FIG. **11** except that units SOR 4/5 and SOR 5/7 have a reverse configuration.

FIG. **14** is similar to FIG. **12** except that SOR 4/5 is removed such that a mixture of linear and methyl-branched compounds proceeds through the process. The final product is a mixed linear and methyl-branched primary OXO alcohol.

FIG. **15** is similar to FIG. **13** except that SOR 4/5 is removed such that a mixture of linear and methyl-branched compounds proceeds through the process. The final product is a mixed linear and methyl-branched primary OXO alcohol.

FIG. **16** is similar to FIG. **10** except that the plant is fitted such that the olefinic branched-enriched stream, **55**, can be used to make either modified alkylbenzene and/or modified primary OXO alcohols.

FIG. **17** is similar to FIG. **11** except that the plant is fitted such that methyl-branched olefin stream **54** can be used to make either modified alkylbenzene and/or modified primary OXO alcohols.

FIG. **18** is similar to FIG. **14** except that the plant is fitted such that methyl-branched and linear olefin stream **61** can be used to make product comprising modified alkylbenzene and/or modified primary OXO alcohols along with the corresponding linear counterparts.

SUMMARY OF THE INVENTION

In preferred embodiments, this invention relates to processes for preparing modified alkylbenzenesulfonate surfactants or modified primary OXO alcohols and surfactants derivable therefrom, or even combinations of these different surfactant types. The processes start from hydrocarbon feeds defined in more detail elsewhere herein. "Modified" connotes a very particular type of branching. Specifically, for example, in the context of the OXO alcohols herein, "modified" means that there is methyl branching in positions other than the usual OXO position, while substantially avoiding branching in positions or of types that would adversely affect biodegradation Preferred "modified" refers to mid-chain positioned, mono-lower alkyl, especially monomethyl substitution of the OXO alcohol. The processes comprise (a) a particularly defined adsorptive separation stage and, when making modified alkylbenzenes and/or alkylbenzenesulfonates, (c) an alkylation stage. Of significant utility for the manufacturer of detergents, the hydrocarbon feed can be an adsorptive separation raffinate or effluent deriving from a linear alkylbenzene manufacturing process or conventional linear detergent alcohol process, though other feeds, such as jet/diesel or olefins can be used.

When the feed is paraffinic, process embodiments typically and preferably further include (b) a dehydrogenation stage inserted in the sequence between the adsorptive separation and the alkylation and, when a modified alkylbenzene is the desired product, (c) an alkylation stage. When the feed is olefin, quite evidently, dehydrogenation is not essential. In general, the alkylation stage is preferably followed by (d) sulfonation; (e) neutralization; and (f) formulation into consumer cleaning products by mixing, agglomeration, compaction, spray-drying and the like. Any stage can have more than one step and include options such as distillation, provided that it includes at least the specified minimum

When making a modified alkylbenzene, stage (a), adsorptive separation, comprises at least partially separating the hydrocarbon feed selected from olefinic feeds, paraffinic feeds and mixed olefinic/paraffinic feeds, into at least one branched-enriched stream comprising an increased proportion (e.g., in relative terms at least about 50% higher, and in absolute terms, that is in terms of percentage by weight, at least about 10% by weight) of branched acyclic hydrocarbons relative to said hydrocarbon feed and typically, one or more additional streams, for example at least one linear-enriched stream comprising an increased proportion (e.g., in relative terms at least about 50% higher, and in absolute terms at least about 10% by weight) of linear acyclic aliphatic hydrocarbons relative to said hydrocarbon feed. Other streams present in the process can vary in composition. Such streams include reject streams, in which cyclic and/or aromatic undesirable components from the feeds are present at levels generally exceeding those of the feed; recycle streams and the like can also be present.

In more detail, the adsorptive separation part, (a), of the process has one or more steps comprising first, providing the hydrocarbon feed, then at least one step selected from adsorptive separation using porous media (preferred), clathration using a clathrating compound selected from urea, thiourea and alternative clathrating amides; and combinations thereof This stage uses simulated moving bed adsorptive separation means known from the art (see in particular U.S. Pat. No. 2,985,589 incorporated herein in its entirety) comprising both of at least one bed holding said porous media or clathrating compound (see, for example FIG. 1 of U.S. Pat. No. 2,985,589 and the associated description) and a device, typically a rotary valve of a highly specialized design, for simulating motion of said porous media or clathrating compound countercurrent to a hydrocarbon stream in said bed. (see in particular U.S. Pat. No. 2,985,589 FIG. 2).

Particularly unusual and novel in the context of the present process is that, at minimum, the simulated moving-bed adsorptive separation herein is used to obtain an essential branched-enriched stream, that is, the exact opposite of the practice used in linear alkylbenzenesulfonate surfactant manufacture. This essential difference is also associated with having a different content of the bed as compared to conventional practice, that is, there is at least one bed containing porous media differing from the 4–5 Angstrom zeolites normally used for linear alkylbenzene manufacture by having larger pore size and reconfiguring the process equipment, notably said bed and said device, so that they connect differently with the associated process steps. More specifically, these means are configured such that the branched stream is passed on through the process, while any linear-enriched streams, however useful for other purposes, are either rejected from the present process or are present in accompaniment of branched-enriched streams. Moreover, stage (a) of the instant process (or stage (A), when making modified primary OXO alcohols) suitably comprises use of at least one porous medium selected from the group consisting of porous media having a minimum pore size at least larger than the pore size required for selective adsorption of linear acyclic hydrocarbons, said pore size not exceeding about 20 Angstroms, more preferably not exceeding about 10 Angstroms.

When said hydrocarbon feed comprises more than about 10% of paraffins, and invariably with higher levels, e.g., about 11% to 90% or higher of paraffins, the present process preferably includes an additional step, (b), of at least partially dehydrogenating said branched-enriched stream. Dehydrogenation can be done using known catalysts and conditions.

When making modified alkylbenzenes, regardless of the type of feed, the present process preferably comprises (c) reacting a branched-enriched stream prepared by one or both of the preceding steps (adsorptive separation optionally with dehydrogenation provided that the branched-enriched stream ultimately comprises olefin, typically at least about 5%, more typically at least about 15% of olefins, generally 5% to 90% or higher) with an aromatic hydrocarbon selected from benzene, toluene and mixtures thereof in the presence of an alkylation catalyst. The preferred alkylation step herein has a low internal isomer selectivity of from 0 to no more than about 40, preferably no more than about 20, and is described and defined more fully elsewhere herein. Such low selectivity alkylations are believed novel in their own right in the context of modified alkylbenzene manufacture.

Preferred processes herein further preferably meet at one least one, and more preferably both, of the following requirements: As the first requirement, said stage (a) means comprise one, two or more of said devices and at least two of said beds, at least one of said beds comprising porous media differentiated relative to the contents of another of said beds by an increased capacity to retain methyl-branched acyclic aliphatic hydrocarbons. For example, zeolites having pore size of above about 5 to no more than about 7 Angstrom are especially preferred. As the second requirement, when making modified alkylbenzenes, said step. (c) has an internal isomer selectivity of from 0 to no more than about 40, preferably lower as further defined hereinafter.

Preferred processes herein operate in a manner contradictory to and inconsistent with conventional practice for making alkylbenzenesulfonate surfactants, which accept linear materials for further processing and reject most branched materials. Further, in order to achieve this reversal, it is found necessary to make use of an unconventional interconnection of adsorptive separation operations as further described and illustrated in the Figures of this specification.

Also in preferred processes herein, said simulated moving bed adsorptive separation means in said stage (a) comprise not one, but two of said devices The number of devices taken in conjunction with their configuration is of especial importance in accomplishing the manufacture of the preferred compositions of the invention and increases specific types of branching in the hydrocarbon streams.

Further, in certain preferred processes having two of said beds, each comprises a different member of said porous media, each of said beds being controlled by one of said devices, and each of said devices having a minimum of eight ports (as defined in U.S. Pat. No. 2,985,589) for achieving simulated movement of said porous media in said beds. Each of said beds is further preferably divided into a vertically positioned array of at least eight sub-beds. (See FIG. 1 in U.S. Pat. No. 2,985,589). Also preferably, stage (a) uses exclusively porous media, rather than clathrating compounds, in said beds.

Processes herein when making modified alkylbenzenes, can have one or more steps following the alkylation step. Such steps can include the additional step of (d) sulfonating the product of step (c).

Sulfonation can be followed by the additional step of (e) neutralizing the product of step (d). Such steps can be followed by (f) mixing the product of step (d) or (e) with one or more cleaning product adjunct materials; thereby forming a cleaning product.

The present invention also encompasses modified alkylbenzene produced by any of the processes herein, as well as modified alkylbenzenesulfonic acid or modified alkylbenzenesulfonate surfactant in any known salt form such as the sodium form, the potassium form, the ammonium form, the substituted ammonium form or the like, produced by any of the processes herein, as well as consumer cleaning products produced by any of the processes herein

Likewise, when producing anionic surfactants from modified primary OXO alcohols as taught herein, all the above identified salt forms of the surfactants are encompassed by the invention.

Cleaning product embodiments herein, whether they incorporate the modified alkylbenzene sulfonates and/or any of the modified primary OXO alcohol derived surfactants taught herein, include laundry detergents, dishwashing detergents, hard surface cleaners and the like. In such embodiments, the content of modified surfactants produced by the instant process is from about 0.0001% to about 99.9%, typically from about 1% to about 50%, and the composition further comprises from about 0.1% to about 99.9%, typically from about 1% to about 90%, of cleaning product adjunct materials such as cosurfactants, builders, enzymes, bleaches, bleach promoters, activators or catalysts, and the like.

The present invention also has alternate embodiments using paraffinic hydrocarbon feeds, in which two adsorptive separations, particularly configured in much the same manner as stage (a) described herein for modified alkylbenzene production, are followed by additional steps other than benzene alkylation step (c), and lead to useful cleaning surfactants. Such steps replacing the step (c) alkylation can include at least one step selected from: dehydrogenation, chlorination, sulfoxidation, oxidation to a C8–C20 alcohol and oxidation to a C8–C20 carboxylic acid or salt thereof, optionally followed by one of: glucosamidation, conversion to a nonsaccharide-derived amide surfactant (for example a monoethanolamide surfactant or any such amide not having a glucose moiety), and sulfonation as ester. Other alternative embodiments use a hydrocarbon feed comprising 20% or more of methyl-branched olefins, again, this process has the particularly configured stage (a) adsorptive separations. Subsequent steps can include alkylation with benzene or toluene optionally followed by sulfonation; alkylation with phenol followed by at least one of alkoxylation, sulfation, sulfonation or combinations thereof, hydroformylation to alcohol optionally followed at least one of alkoxylation, glycosylation, sulfation, phosphation or combinations thereof, sulfonation, epoxidation; hydrobromination followed by amination and oxidation to amine oxide; and phosphonation.

The invention also encompasses the surfactants produced by such processes and the cleaning products produced by such processes. The present invention moreover includes especially useful embodiments wherein the adsorptive separations of stage (a) comprise at least one separation step using an organometallic-grafted mordenite such as a tin-grafted mordenite. The invention also encompasses a method comprising use of a grafted mordenite for manufacturing detergent surfactants and any of the corresponding surfactants and consumer products produced by use of these specific porous media in any of the above-defined processes.

The present invention has many other important embodiments and ramifications. Thus the present invention encompasses a process comprising: (A) a stage of at least partially separating a hydrocarbon feed comprising branched aliphatic hydrocarbons, more particularly, paraffinic hydrocarbons, having from about 8 to about 20 carbon atoms, into at least one branched-enriched stream comprising an increased proportion of branched acyclic hydrocarbons relative to said hydrocarbon feed and optionally, one or more of:

a linear-enriched stream comprising an increased proportion of linear aliphatic hydrocarbons relative to said hydrocarbon feed; and

a reject stream comprising cyclic and/or aromatic and/or ethyl- or higher-branched hydrocarbons;

wherein said stage (A) comprises:

providing said hydrocarbon feed; and

adsorptive separation of said feed into said streams using porous media; said stage (A) using simulated moving bed adsorptive separation means comprising both of

at least one bed holding said porous media; and

a device for simulating motion of said porous media countercurrent to a hydrocarbon stream in said bed; followed by further stages (B), (C) and (D) (any of which can have one or more steps) as follows:

(B) (i) at least partially dehydrogenating the branched-enriched stream of stage (A) thereby forming an olefinic branched-enriched stream comprising mono-olefin (optionally large proportions, up to 80% or higher of paraffins may also be present along with impurities such as diolefins and/or aromatic impurities), optionally followed by one or more of (ii) treating said olefinic branched-enriched stream to diminish the content therein of diolefin impurities and (iii) treating said olefinic branched-enriched stream to diminish the content therein of aromatic impurities; (C) optionally, at least partially concentrating said mono-olefins in said olefinic branched-enriched stream of stake (B) by means of sorptive separation using a known sorbent or porous media provided that said sorbent or porous media are nonidentical with the porous media of stage (A) and ale adapted for olefin/paraffin separations (such as, for example, is the case for copper-treated or silver-treated zeolite X or Y) and, optionally, concurrently recycling paraffins to said dehydrogenation stage (B), and

(D) reacting said olefinic branched-enriched stream produced in stage (B) or, optionally, as further concentrated in stage (C), with carbon monoxide and hydrogen in the presence of an OXO catalyst, thereby forming a modified primary OXO alcohol.

In the description of processes herein, the term “stage” refers to a collectively identifiable group of one or more process steps For example, (A) is an adsorptive separation stage, essentially a inodified MOLEX® stage which can be licensed from UOP Corp., here unconventionally configured to enrich (rather than decrease as in normal practice) the branched content of the hydrocarbons. It can optionally include as part of the same stage ancilliary steps such as distillation, addition or removal steps with lower boiling hydrocarbons to wash adsorbent, etc., all as known in the art. (B) is a dehydrogenation stage, comprising, at minimum, a dehydrogenation step but often including other optional steps such as those specifically mentioned supra. Essential process technology for (B) can be licensed from UOP Corp., for example as the PACOL® process. (C) is essentially a conventional OLEX stage, again available from UOP Corp. (D) is preferably an OXO stage of the kind referred to in the art as a “one-step low pressure OXO” and is well-known in the art. As with the other stages of this process, stage (D) can be complemented by other optional steps, for example, catalyst removal, etc. Unless otherwise indicated, the convention herein will be to use capitals (A, B, C . . .) when referring to stages of the present process embodiments wherein the process includes making a modified primary OXO alcohol.

Surfactants derivable from these new modified primary OXO alcohols and the aforementioned alkylbenzenes have significant advantages, such as in being more soluble at a given chainlength/carbon number which is important in view of the growing popularity of low wash temperatures; and in having unexpectedly high rates of dissolution when incorporated into detergent granules. Thus the OXO alcohols and the alkylbenzenes themselves have exceptional utility to the manufacturer of cleaning compositions such as heavy-duty laundry detergents, dishwashing liquids and the like. All percentages, ratios and proportions herein are by weight, unless otherwise specified. All temperatures are in degrees Celsius (° C.) unless otherwise specified. All documents cited are in relevant part, incorporated herein by reference.

DETAILED DESCRIPTION OF THE INVENTION

In one embodiment, the present invention relates to a process for preparing a modified alkylbenzenesulfonate surfactant from a hydrocarbon feedstock. The equivalent terms “feed” and/or “feedstock” are used herein to identify any hydrocarbon useful as a starting material in the present process. In contrast, the term "stream" is typically used to identify hydrocarbon which has undergone at least one process step. The hydrocarbon feed herein in general contains useful proportions of acyclic aliphatic hydrocarbons, whether olefinic or paraffinic, or may include mixtures of such olefins and paraffins. The raw feedstock further typically includes varying amounts of cyclic and/or aromatic impurities, as found for example in kerosene, jet/diesel (middle distillate) hydrocarbon cuts. In the feedstock, the olefins and paraffins generally occur in both branched and linear forms. Moreover, in general, the branched forms in the feedstock can be either undesirable or desirable for the present purposes. The present purposes of providing cleaning products differ markedly, for example, from gasoline manufacture in which a high degree of polymethyl-branched hydrocarbons is desirable for increasing octane rating The present invention provides processes for separating particular desired forms of the hydrocarbon feeds for cleaning product purposes, and of incorporating them into surfactants (especially certain modified alkylbenzene sulfonates and/or surfactants based on modified primary OXO alcohols) and into cleaning products and useful surfactant intermediates for such products.

The term "modified" as applied in connection with any product of the present process means that the product contains a very particular type of branching and surprisingly departs from the linear structure which is now commonly taught to be preferred and used for cleaning product surfactants. The term "modified" is further used to differentiate the products herein from conventional highly-branched cleaning surfactant structures, such as those found in tetrapropylene benzene sulfonates, and from all other conventional branched structures such as "two-tailed" or "Guerbet" or aldol-derived branched structures.

Hydrocarbon feeds herein can in general vary quite widely, but typically include methyl branches such as monomethyl, dimethyl (including gem-dimethyl), trimethyl, polymethyl, ethyl, and higher alkyl branches The hydrocarbon feeds may contain quaternary carbon atoms. However, tolerance for quaternary carbon atoms in the feeds is much superior when the present processes include an alkylation stage as taught hereinafter. Preferred feeds herein in embodiments of the invention which have an OXO process stage and do not have an alkylation stage are essentially free from quaternary carbon atoms. The desirable components for the present purposes include monomethyl-branched, dimethyl-branched other than gem-dimethyl-branched, and to some extent, especially at carbon contents in excess of about 4, some proportion of trimethyl-branched. The hydrocarbon feeds include useful proportions, e.g., 5%–40% or more, of acyclic hydrocarbons having in general from about 9 to about 20 carbon atoms depending on the desired type of cleaning product surfactant or the cleaning product use of the modified surfactant being produced. More preferably, when making modified alkylbenzenes and modified alkylbenzenesulfonates the acyclic aliphatic hydrocarbons of the feedstock comprise from about 10 to about 16, more preferably from about 11 to about 14 carbon atoms.

The present processes comprise a particularly defined adsorptive separation stage and, for the purposes of making modified alkylbenzenes and alkylbenzenesulfonates, an alkylation stage is also essential. When the feedstock is paraffinic, process embodiments typically and preferably further include a dehydrogenation stage inserted in the sequence between the adsorptive separation and the alkylation, or, when making modified primary OXO alcohols, between the adsorptive separation of type referred to as SOR 4/5 or SOR 5/7 in the Figures, and the OXO process stage In general, the alkylation or OXO stage can be followed by additional steps such as sulfonation, typically followed by neutralization and formulation into consumer cleaning products by mixing, agglomeration, compaction, spray-drying and the like. Also in general, any stage can have more than one step provided that it includes at least the minimum of one step.

Stage (a), adsorptive separation, comprises at least partially separating the hydrocarbon feed selected from olefinic feeds, paraffinic feeds and mixed olefinic/paraffinic feeds into at least one branched-enriched stream comprising an increased proportion (e.g., in relative terms compared to the feed at least about 50% higher, more preferably at least about 100% higher, typically treble, quadruple or more and in absolute terms, that is in terms of percentage by weight, at least about 10% by weight, typically at least 20%, more preferably from 30% to about 90% or more) of branched acyclic hydrocarbons (especially the desired types identified supra, particularly methyl-branched paraffins or methyl-branched mono-olefins) relative to said hydrocarbon feed and optionally, one or more of: a linear-enriched stream comprising an increased proportion (e.g., in relative terms at least about 50% higher, more preferably at least about 100% higher, typically treble, quadruple or more and in absolute terms at least about 10% by weight, typically at least 20%, more preferably from 30% to about 90% or more) of linear acyclic aliphatic hydrocarbons relative to said hydrocarbon feed; and a reject stream comprising cyclic and/or aromatic hydrocarbons or other impurities such as gem-dimethyl hydrocarbons, ethyl-branched hydrocarbons or higher-branched hydrocarbons.

Other streams present anywhere in the present process can vary in composition. Such streams include reject streams, in which cyclic and/or aromatic undesirable components from the feeds are present at levels generally exceeding those of the feed; recycle streams having compositions depending on the parts of the process they connect, and the like. Known processes, such as that of U.S. Pat. No. 5,012,021 or U.S. Pat. No. 4,520,214 both incorporated by reference, can be used herein to convert impurities, such as certain diolefins, back to monoolefins using a selective catalyst. Other processes which can optionally be incorporated herein to selectively remove aromatic by-products formed in paraffin dehydrogenation include those of U.S. Pat. No. 5,300,715 and U.S. Pat. No. 5,276,231 involving the use of one or more aromatic removal zones and/or extractants for aromatics which may include, for example, sulfolane and/or ethylenediamine.

In more detail, the adsorptive separation stage or part of the process used to enrich the content of branched hydrocarbons in the feed has one or more steps comprising at least one step selected from providing a suitable hydrocarbon feed and at least one step selected from adsorptive separation using porous media, clathration using a clathrating compound selected from urea, thiourea and alternative clathrating amides, and combinations thereof. Very preferably, when using combinations, at least one step is an adsorptive separation using porous media of the larger-pore type described more fully hereinafter. Stage (a) (or stage (A) when making modified primary OXO alcohols) uses simulated moving bed adsorptive separation means well known from the art (see in particular U.S. Pat. No. 2,985,589 incorporated herein in its entirety) comprising both of at least one bed holding said porous media or clathrating compound (see, for example U.S. Pat. No. 2,985,589 FIG. 1 and the associated description) and a device for simulating motion of said porous media or clathrating compound countercurrent to a hydrocarbon stream in said bed. (See in particular U.S. Pat. No. 2,985,589 FIG. 2 and the associated description, or variants in current commercial use for the production of linear alkylbenzenesulfonates). The device in question is typically a rotary valve of a highly specialized design. In general, types of such valves as used in current linear alkylbenzene manufacture can be used herein. Adsorptive separation conditions, e.g., pressures, temperatures and times, can be as used in the art. See, for example, U.S. Pat. No. 2,985,589.

What is particularly unusual and novel in the context of the present process is that, at minimum, the simulated moving-bed adsorptive separation herein: is used to obtain an essential branched-enriched stream, that is, the exact opposite of the practice used in linear alkylbenzenesulfonate surfactant manufacture. This essential difference is also associated with changing the contents of the bed so that it contains porous media differing from the 4–5 Angstrom zeolites normally used for linear alkylbenzene manufacture, and reconfiguring the process equipment, notably said bed and said device, so that they connect differently with the associated process steps More specifically, these means are configured such that the branched stream is passed on through the process, while any linear-enriched streams, however useful for other purposes, are either rejected from the present process or are present in accompaniment of branched-enriched streams.

When said hydrocarbon feed comprises less than about 5% of olefins, the present process preferably includes an additional stage, (b), or stage (B) when making modified primary OXO alcohols, of at least partially dehydrogenating the product of stage (a). Dehydrogenation can be done using any known dehydrogenation catalyst, such as the De-H series from UOP, and are further illustrated hereinafter. Dehydrogenation conditions are similar to those used in current linear alkylbenzenesulfonate manufacture.

When making modified alkylbenzenes, regardless of the type of feedstock treated, the present process preferably comprises (c) reacting the product of stage (a), or when stage (b) is also present in the foregoing steps, the product of stage (a) followed by stage (b), with an aromatic hydrocarbon selected from benzene, toluene and mixtures thereof in the presence of an alkylation catalyst The preferred alkylation step herein has a low internal isomer selectivity of from 0 to about 40, preferably not more than about 20, more preferably not more than about 10, as described and defined more fully elsewhere herein. Such low internal isomer selectivities are believed novel in their own right.

In one mode, the alkylation step herein is run in the presence of excess paraffin, which is then recovered and recycled to the dehydrogenator. In another mode, the alkylation step is run in presence of 5× to 10× excess of arene. Any combination of such modes is possible.

Note that when the final branched-enriched stream, i. e., the product of stage (a), has appreciable olefin content, e.g., more than about 5% olefins in total, this stream can proceed directly to the alkylation step (c), then recovered paraffins can be recycled to a dehydrogenation reactor for at least partial conversion to olefin. See, for example, FIGS. **5**, **6**, **7**.

Of great importance to the present invention, preferred processes herein further preferably meet at one least one, and more preferably both, of the following requirements: As the first requirement, said stage (a) means (or, when making modified primary OXO alcohols, stage (A) means) comprise one, two or more of said devices (e.g., the aforementioned rotary valves or any equivalent means) and at least two of said beds, at least one of said beds comprising, porous media differentiated relative to the contents of another of said beds by an increased capacity to retain methyl-branched acyclic aliphatic hydrocarbons. For example, zeolites having pore size at least in excess of sizes used in conventional linear alkylbenzene manufacture and up to about 20 Angstrom, more preferably up to about 10 Angstrom, more preferably still up to about 7 Angstrom, or other porous media such as certain silicoaluminophosphates or Mobil MCM-type materials are suitable herein provided that the pore sizes are as noted. When using porous materials having pore sizes above about 7 Angstrom, it is often highly desirable to "tune down" the pore openings, for example by grafting of tin alkyls at the pore openings. See EP 559,510 A incorporated herein by reference in its entirety As the second requirement, when making modified alkylbenzenes, said step (c) has an internal isomer selectivity of from 0 to no more than about 40, preferably lower, as noted supra and as further defined in detail hereinafter.

In other preferred processes, at least one of said beds comprises porous media conventional for the manufacture of linear alkylbenzenes, said beds being connected into said process in a manner consistent with at least partially increasing the proportion of methyl-branched acyclic aliphatic hydrocarbons in streams passing to step (c) of said process, and at least partially decreasing the proportion of linear acyclic aliphatic hydrocarbons passing to step (c) of said process, said linear acyclic aliphatic hydrocarbons being at least partially removed as reject stream in stage (a). In other words, preferred processes herein operate in a manner contradictory to and inconsistent with conventional practice for making alkylbenzenesulfonate surfactants, which reject branched materials and accept linear materials for further processing. Further, in order to achieve this reversal, it is found necessary to make use of an unconventional interconnection of adsorptive separation operations as already briefly described and as further illustrated in the Figures herein.

Also of great importance, in preferred processes herein, said simulated moving bed adsorptive separation means in said stage (a) (or stage (A) when making modified primary OXO alcohols) comprise not one, but two of said devices, or a single device capable of simulating movement of said porous media in at least two independent beds. In other words, for all preferred processes herein, using a single device, for example a device as taught in U.S. Pat. No. 2,985,589, will not suffice. The number of devices taken in conjunction with their configuration is of especial importance in accomplishing the manufacture of the preferred compositions of the invention. Thus, in a hypothetical not known from the art, an increasing purification of a linear hydrocarbon might be accomplished by two devices and two beds connected in series. A highly linear adsorbate of the first stage might proceed to a second stage adsorptive separation process inlet for further purification. Such a configuration is outside the present invention on account of its incorrect connection of the stages, which lead to increasing the linearity and purity of a hydrocarbon. The present processes, as has already been noted, involve passing branched streams though the various steps or stages, requiring a connection of the devices which is consistent with the objective. This increases specific types of branching in the hydrocarbon streams herein.

Further of great importance in preferred processes herein, there are two of said beds, each comprising a different member of said porous media, each of said beds being controlled by one of said devices, and each of said devices having la minimum of eight ports for achieving simulated movement of said porous media in said beds. Each of said beds is further preferably divided into a vertically positioned array of at least eight sub-beds. Also preferably, stage (a) uses exclusively porous media in said beds. Thus, the invention can make use of conventional beds and devices of the general type described in U.S. Pat. No. 2,985,589; but their number and connection into the present process is novel and unprecedented in alkylbenzenesulfonate manufacturing plants

Also, the better to illustrate what has already been described, in certain embodiments of preferred processes herein, said linear-enriched stream is present in stage (a) and stage (a) comprises: (a-i) adsorptive separation of said hydrocarbon feed into said 1linear-enriched stream and an intermediate branched-enriched stream and rejection of said linear-enriched stream for essential purposes of said process, by means of one of said simulated moving beds, followed by (a-ii) adsorptive separation of said intermediate branched-enriched stream into said branched-enriched stream comprising an increased proportion of branched (more particularly methyl-branched) acyclic aliphatic hydrocarbons relative to said linear-enriched stream, and a reject stream comprising at least an increased proportion of cyclic and/or aromatic hydrocarbons relative to said branched-enriched stream, by means of another of said simulated moving beds.

Said reject stream in said step (a-ii) can further comprise: undesired branched hydrocarbons selected from gem-dimethyl branched hydrocarbons, ethyl branched hydrocarbons and higher than ethyl branched hydrocarbons, and :wherein the acyclic aliphatic hydrocarbons of said intermediate branched-enriched stream and said branched-enriched stream comprise a reduced proportion of said gem-dimethyl branched hydrocarbons, ethyl branched hydrocarbons and higher than ethyl branched hydrocarbons relative to said hydrocarbon feed. In terms of tolerance of these various components in the intermediate branched-enriched stream, ethyl branched hydrocarbons are much more acceptable than are gem-dimethyl, cyclic and aromatic components. In general, a minimum of "increasing proportion", "decreasing proportion", or "enriching" of any component in any step herein corresponds to any increase (enrichment) or decrease in proportion useful for the practically stated purposes of the invention. Such amounts are well illustrated throughout the specification.

Also in said process, said stream compositions can be achieved by selecting as said porous media: a member selected from the group consisting of 4–5. Angstrom pore-size zeolites in said step (a-i) and a member selected from the group consisting of porous media having a pore size at least greater than about the maximum pore size of said step (a-i) zeolite and at most about 10 Angstrom in said step (a-ii)

In another preferred embodiment, stage (a) comprises: (a-i) adsorptive separation of said hydrocarbon feed into an acyclic aliphatic hydrocarbon-enriched stream comprising linear- and branched (such as the desirable types described supra) acyclic aliphatic hydrocarbons and a first reject stream comprising at least an increased proportion of cyclic and/or aromatic hydrocarbons relative to said hydrocarbon feed, followed by (a-ii) adsorptive separation of said acyclic aliphatic hydrocarbon-enriched stream into said branched-enriched stream and said linear-enriched stream; wherein said adsorptive separations are accomplished using said simulated moving bed adsorptive separation means. Unless otherwise noted herein, the "branched-enriched stream" is the final stream of stage or step (a); additional qualifiers such as "intermediate" will otherwise be prefixed on the name to indicate that the stream, though enriched in branched hydrocarbons, requires further treatment before proceeding from the adsorptive separation stages of the instant process to other stages. Also to be noted, stage (a), the adsorptive separation stage, can freely include other conventional, optional steps, such as:distillation, provided that adsorptive separation is conducted. Thus, current commercial MOLEX® plants will typically further include distillation in this stage and can be useful herein.

The invention further encompasses a process wherein said first reject stream in said step (a-i) further comprises undesired branched hydrocarbons selected from gem-dimethyl branched hydrocarbons, ethyl branched hydrocarbons and higher than ethyl branched hydrocarbons; and wherein said acyclic aliphatic hydrocarbon-enriched stream and said branched-enriched stream each comprises a reduced proportion of said gem-dimethyl branched hydrocarbons, ethyl branched hydrocarbons and higher than ethyl branched hydrocarbons relative to said hydrocarbon feed. In such embodiments, stream compositions can be achieved by selecting as said porous media a member selected from the group consisting of 4–5 Angstrom pore-size zeolites in said step (a-ii) and a member selected from the group consisting of porous media having a pore size at least greater than about the maximum pore size of said step (a-ii) zeolite and at most about 10 Angstrom in said step (a-i).

More generally, the invention relates to a process wherein stage (a) comprises use of at least one porous medium selected from the group consisting of porous media having a minimum pore size larger than the pore size required for selective adsorption of linear acyclic hydrocarbons, said pore size not exceeding about 20 Angstroms.

As noted, preferred processes herein include those wherein said alkylation step, (c), has an internal isomer selectivity of from 0 to 20; also, a preferred alkylation step, (c) uses an alkylation catalyst consistent with said internal isomer selectivity, and wherein said alkylation catalyst is selected from the group consisting of at least partially acidic mordenites and at least partially acidic zeolite beta. Preferred alkylation catalysts include H-mordenites and H-beta, more preferably H-mordenite, which is at least partially dealuminized.

With respect to making modified alkylbenzenes and modified alkylbenzenesulfonates, the invention also preferably includes the process wherein said hydrocarbon feed comprises at least about 10% methyl-branched paraffins having molecular weight of at least about 128 and no more than about 282, said process having said dehydrogenation step (b) More preferably in such embodiments, said hydrocarbon feed comprises at least about 20% methyl-branched paraffins having molecular weight of at least about 128 and no more than about 226; said process having said dehydrogenation step (b) and having alkylation step (c); and also preferably includes the process wherein said hydrocarbon feed comprises at least about 10% methyl-branched olefins having molecular weight of at least about 126 and no more than about 280. More preferably in such embodiments, the hydrocarbon feed comprises at least about 50% methyl-branched olefins having molecular weight of at least about 126 and no more than about 224; said process having no dehydrogenation step (b).

For the corresponding processes wherein a modified primary OXO alcohol is made, the above ranges can be extended somewhat, consistent with going to a total carbon number of up to about C20 or higher. More preferably, the upper-end paraffin molecular weight of 226 supra is extended to about 254, and the upper-end olefin molecular weight of 224 supra is extended to about 252.

Of significant utility for the manufacturer of detergents, the hydrocarbon feed or feedstock herein can be an adsorptive separation raffinate or effluent deriving from a linear alkylbenzene manufacturing process, or from a conventional linear detergent alcohol process.

Processes herein can have one or more steps following the alkylation step. Such steps can include the additional step of (d) sulfonating the product of step (c).

Sulfonation can be followed by the additional step of (e) neutralizing the product of step (d). Such steps can be followed by (f) mixing the product of step (d) or (e) with one or more cleaning product adjunct materials; thereby forming a cleaning product.

Thus the process herein includes highly preferred embodiments having all of the additional steps of (d) sulfonating the modified alkylbenzene product of step (c); (e) neutralizing the modified alkylbenzenesulfonic acid product of step (d); and (f) mixing the modified alkylbenzenesulfonic acid or modified alkylbenzenesulfonate surfactant product of steps (d) or (e) with one or more cleaning product adjunct materials thereby forming a cleaning product in one such embodiment, prior to said sulfonation step, modified alkylbenzene which is the product of said step (c) is blended with a linear alkylbenzene produced by a conventional process. In another such embodiment, in any step subsequent to said sulfonation step, modified alkylbenzene sulfonate which is the product of said step (d) is blended with a linear alkylbenzene sulfonate produced by a conventional process. In these blended embodiments, a preferred process has a ratio of modified alkylbenzene to linear alkylbenzene of from about 1:100 to about 100:1. When a relatively more linear product is desired, a preferred ratio is from about 10:90 to about 50:50 When a relatively more branched product is desired, a preferred ratio is from about 90:10 to about 51:49.

The present invention also encompasses modified alkylbenzene produced by any of the processes herein; as well as modified alkylbenzenesulfonic acid or modified alkylbenzenesulfonate surfactant in any known salt form such as the sodium form, the potassium form, the ammonium form, the substituted ammonium form or the like, produced by any of the processes herein; as well as consumer cleaning product produced by any of the processes herein.

Cleaning product embodiments herein include laundry detergents, dishwashing detergents, hard surface cleaners and the like. In such embodiments, the content of modified alkylbenzenestilfonate, or content of any surfactant derived from modified primary OXO alcohols, etc., herein and produced by the instant process, is from about 0.0001% to about 99.9%, typically from about 1% to about 50%, and the composition further comprises from about 0.1% to about 99.9%, typically from about 1% to about 50%, of cleaning product adjunct materials such as cosurfactants, builders, enzymes, bleaches, bleach promoters, activators or catalysts, and the like.

Preferred consumer cleaning products produced by these processes suitably comprise from about 1% to about 50% of said modified surfactant and from about 0.0001% to about 99% of cleaning product adjunct materials selected from enzymes, nonphosphate builders, polymers, activated bleaches, catalyzed bleaches, photobleaches and mixtures thereof.

Alternate Process Embodiments

The present invention has alternate embodiments in which two particularly configured adsorptive separations are followed by additional steps which lead to useful cleaning surfactants. Thus, there is encompassed herein a process comprising: (I) separating a hydrocarbon feedstock into a branched hydrocarbon-enriched stream comprising, more preferably consisting essentially of, at least about 85% of saturated acyclic aliphatic hydrocarbons having a carbon content of from about C8 to about C20, said branched hydrocarbon-enriched stream comprising at least about 10% of paraffins having methyl branches, said methyl branches being distributed in said paraffins such that any paraffin molecule has from 0 to no more than about 3 of said methyl branches and said branches being positioned within said paraffins to an extent that at least about 90% of said branches occupy positions other than those forming gem-dimethyl and/or quaternary moieties; wherein said separation is conducted by means including at least two adsorptive separation steps using simulated moving bed adsorptive separation means and at least two porous media having different pore sizes; and (II) converting said branched hydrocarbon enriched stream to a surfactant by further steps including at least one step selected from. dehydrogenation, chlorination, sulfoxidation, oxidation to a C8–C20 alcohol and oxidation to a C8–C20 carboxylic acid or salt thereof, optionally followed by one of: glucosamidation, conversion to a nonsaccharide-derived amide surfactant and sulfonation as ester.

Further by way of alternate embodiments, there is encompassed herein a process comprising: (I) separating a hydrocarbon feedstock into a olefinic branched hydrocarbon-enriched stream comprising, preferably consisting essentially of, mixtures of olefinic acyclic aliphatic hydrocarbons having a carbon content of from about C8 to about C20 or mixtures thereof with their saturated analogs, said branched hydrocarbon-enriched stream comprising at least about 10% of the sum of said olefins and their saturated analogs having methyl branches, said methyl branches being distributed in said mixtures such that any of said acyclic aliphatic hydrocarbon molecules has from 0 to no more than about 3 of said methyl branches and said branches being positioned within said acyclic aliphatic hydrocarbon molecules to an extent that at least about 90% of said branches occupy positions other than those forming gem-dimethyl moieties, wherein said separation is conducted by means including at least two adsorptive separation steps using simulated moving bed adsorptive separation means and at least two porous media having different pore sizes; and (II) converting said olefinic branched hydrocarbon enriched stream to a surfactant by further steps including at least one step selected from: alkylation with benzene or toluene optionally followed by sulfonation; alkylation with phenol followed by at least one of alkoxylation, sulfation, sulfonation or combinations thereof, hydroformylation optionally followed at least one of alkoxylation, alkoxylation combined with oxidation, glycosylation, sulfation, phosphation or combinations thereof, sulfonation; epoxidation; hydrobromination followed by amination and oxidation to amine oxide; and phosphonation.

In view of the alternate processes encompassed, the invention also encompasses the surfactants produced by such processes and the cleaning products produced by such processes.

Aspects of the invention will now be discussed and illustrated in more detail.

Modified Alkylbenzenes and Alkylbenzenesulfonate Products

As noted in summary, the present invention includes a process for preparing modified alkylbenzenesulfonate surfactants suitable for use in cleaning products such as laundry detergents, hard surface cleaners, dishwashing detergents and the like.

The terms "modified alkylbenzenesulfonate surfactant" and "modified alkylbenzene" refer products of the processes herein The term "modified" as applied either to the novel alkylbenzenesulfonate surfactants or to the novel alkylbenzenes (MAB) is used to indicate that the product of the present process is compositionally different from that of all alkylbenzenesulfonate surfactants hitherto used in commerce in consumer cleaning compositions. Most particularly, the instant compositions differ compositionally from the so-called "ABS" or poorly biodegradable alkylbenzenesulfonates, and from the so-called "LAS" or linear alkylbenzenesulfonate surfactants Conventional LAS surfactants are currently commercially available through several processes including those relying on HF-catalyzed or aluminum chloride-catalyzed alkylation of benzene. Other commercial LAS surfactants include LAS made by the DETAL® process. Preferred alkylbenzenesulfonate surfactants herein made using the preferred low-internal isomer selectivity alkylation step herein are also compositionally different from those made by alkylating linear olefins using fluoridated zeolite catalyst systems, believed also to include fluoridated mordenites. Without being limited by theory, it is believed that the modified alkylbenzenesulfonate surfactants herein are uniquely lightly branched. They typically contain a plurality of isomers and/or homologs. Often, this plurality of species (often tens or even scores) is accompanied by a relatively high total content of 2-phenyl isomers, 2-phenyl isomer contents of at the very least 25% and commonly 50% or even 70% or higher being attained. Moreover the modified alkylbenzenesulfonate products herein differ in physical properties from known alkylbenzenesulfonate surfactants, for example by having improved surfactant efficiency and low tendency to phase-separate internal isomers from solution, especially in presence of water hardness.

Feeds and Streams of the Process

The term "feed" is used herein to identify a material which has not yet been processed by the present process. The term feed" however may also be used when a step which is optional in the present process (e.g., adsorptive separation over 5 Angstrom Ca-zeolite) has been applied to such a material, provided that such treatment occurs before the first essential step of the present process.

The term "stream" is used herein to identify materials which have undergone at least one step of the present process.

The term "branched-enriched stream" herein unless more particularly noted, refers to any processed hydrocarbon fraction containing at least the smaller of the following:

(i) in relative terms, an increase of at least about 10%, preferably at least 100% (that is, a doubling), more preferably a trebling, quadrupling or more, of branched acyclic C8 to about C20 hydrocarbons, compared to a parent fraction or feed which has not been processed in the present process; or

(ii) in absolute terms, at least about 5%, preferably 10% or more, of branched acyclic C8 to about C20 hydrocarbons, more preferably of about C10 to about C14 hydrocarbons when the process produces modified alkylbenzenes or modified alkylbenzenesulfonates.

The branched hydrocarbons referred to can be olefinic, paraffinic or mixed olefin/paraffin in any proportion unless otherwise more particularly noted. (Certain preferred processes involving making modified primary OXO alcohols as illustrated in FIGS. **9** and higher start from paraffinic feeds, though, more generally, variations of these processes can use olefinic feeds). The branches are preferably monomethyl branches or isolated (non-geminal) dimethyl branches.

The term "linear-enriched stream" herein unless more particularly noted, refers to any processed hydrocarbon fraction which contains a higher percentage by weight of normal (n−) acyclic hydrocarbons than does a parent fraction or feed which has not been processed in the present process.

More particularly, linear-enriched" refers to any processed hydrocarbon fraction containing at least the smaller of the following:

(iii) in relative terms, an increase of at least about 10%, preferably at least 100% (that is, a doubling), more preferably a trebling, quadrupling or more, of linear acyclic C8 to about C20 hydrocarbons, compared to a parent fraction or feed which has not been processed in the present process, or

(iv) in absolute terns, at least about 5%, preferably 10% or more, of linear acyclic C8 to about C20 hydrocarbons.

The linear hydrocarbons can be olefinic, paraffinic or mixed olefin/paraffin in any proportion, unless otherwise more particularly identified.

Qualifiers such as "intermediate" when used in connection with a branched-enriched stream are used to identify that the branched-enriched stream to which is being referred has not completed passage through the adsorptive separation stage (a) of the present process. Other qualifiers such as "olefinic" or "paraffinic" may be used to identify whether the stream contains a preponderance of olefinic or of paraffinic hydrocarbons.

Feeds and streams in the present process both with respect to embodiments comprising alkylation and with respect to embodiments comprising OXO reaction (or concurrent utilization of both) are further illustrated in the following Table. The numbers in the leftmost column refer to the feeds and streams identified in FIG. **1** through FIG. **18**

Stream	Stream Type/ Name	Exemplary Sources (for Feeds) or compositions (for streams)	Predominant Component(s)
1	Hydrocarbon Feed	Jet/Kerosene cuts, preferably from light crudes For process embodiments making modified OXO alcohols, preferred feeds are narrow cuts (e.g., 3, 2, 1 or carbon spread, or nonintegral narrow-cut)	b-paraffin/l-paraffin

-continued

Stream	Stream Type/ Name	Exemplary Sources (for Feeds) or compositions (for streams)	Predominant Component(s)
2	Branched-enriched Stream (Intermediate)	Mainly branched paraffins: still includes cyclics, aromatics	b-paraffin
3	Branched-enriched Stream	Mainly methyl branched paraffins	b-paraffin
4	Branched-enriched Stream (Olefinic)	Mainly methyl branched paraffins; methyl-branched olefins (e.g., at up to about 20%); possibly diolefin impurities will also be present	b-paraffin/b-olefin
5	Modified Alkylbenzene	Mainly methyl-branched alkylbenzenes	Modified Alkylbenzenes produced by FIG. 1 process with alkylation step
6	Linear-enriched Stream	Mainly linear paraffins	1-paraffin
7	Reject Stream (Cyclics/ Aromatics	Cyclics, aromatics, ethyl and higher branched paraffins	
8	Recycle Stream	Mainly methyl-branched paraffins	b-paraffin
9	Hydrocarbon Feed	Jet/Kerosene cuts, preferably from light crudes	b-paraffin/l-paraffin
10	Branched-enriched Stream (Intermediate)	Mainly methyl branched and linear paraffins	b-paraffin/l-paraffin
11	Branched-enriched Stream	Mainly methyl branched paraffins	b-paraffin
12	Branched-enriched Stream (Olefinic)	Mainly methyl branched paraffins; methyl-branched olefins must be present, e.g., at up to about 20%	b-paraffin/l-paraffin
13	Modified Alkylbenzene	Mainly methyl-branched alkylbenzenes	Modified Alkylbenzenes produced by FIG. 2 process with alkylation step
14	Reject Stream (Cyclics/ Aromatics)	Cyclics, aromatics, ethyl- and higher branched paraffins	
15	Linear-enriched Stream	Mainly linear paraffins	l-paraffin
16	Recycle Stream	Mainly methyl-branched paraffins	b-paraffin
17	Hydrocarbon Feed	Jet/Kerosene cuts, preferably from light crudes	b-paraffin/l-paraffin
18	Branched-enriched Stream	Mainly methyl branched and linear paraffins	b-paraffin/l-paraffin
19	Branched-enriched Stream (Olefinic)	Mainly methyl-branched and linear paraffins; must have some linear and methyl branched olefins	b-paraffin/l-paraffin/ b-olefin/l-olefin
20	Linear and Modified Alkylbenzene	Mainly methyl-branched and linear alkylbenzenes	Linear and Modified Alkylbenzene mixture produced by FIG. 3 process
21	Reject Stream	Cyclics, aromatics, ethyl and higher branched paraffins	
22	Recycle Stream	Mainly methyl-branched and linear paraffins	b-paraffin l-paraffin
23	Hydrocarbon Feed	Mixture of branched paraffins and cyclics and aromatics, sourced from conventional LAB plant effluent, e.g., MOLEX ® effluent	b-paraffin
24	Branched-enriched Stream	Mainly methyl branched paraffins	b-paraffin
25	Branched-enriched Stream (Olefinic)	Mainly methyl branched paraffins; methyl-branched olefins must be present, e.g., at up to about 20%	b-paraffin/b-olefin
26	Modified Alkylbenzene	Mainly methyl-branched alkylbenzenes	Modified Alkylbenzenes produced by FIG. 4 process
27	Reject Stream	Cyclics, aromatics, ethyl and higher branched paraffins	
28	Recycle Stream	Mainly methyl-branched paraffins	b-paraffin

-continued

Stream	Stream Type/ Name	Exemplary Sources (for Feeds) or compositions (for streams)	Predominant Component(s)
29	Hydrocarbon Feed	F.T. gasoline, higher cuts; crackate from slack wax; crackate from Flexicoker or Fluidcoker	b-olefin/l-olefin/ b-paraffin/l-paraffin
30	Branched-enriched Stream (Intermediate)	Mainly methyl branched and linear olefins; usually have some linear and methyl branched paraffins	b-olefin/l-olefin/ b-paraffin/l-paraffin
31	Branched-enriched Stream	Mainly methyl branched olefins and methyl branched paraffins; variable ratio	b-olefin/b-paraffin
32	Branched-enriched Stream (Olefinic)	Mainly methyl branched paraffins; methyl branched olefins will present, e.g., at up to 20%	b-paraffin/b-olefin
33	Modified Alkylbenzene	Mainly methyl-branched alkylbenzenes	Modified Alkylbenzenes produced by FIG. 5 process
34	Reject Stream (Cyclics/ Aromatics)	Cyclics, aromatics, ethyl- and higher branched hydrocarbons	
35	Linear-enriched Stream (may include Cyclics/Aromatics)	Mainly linear olefins and linear paraffins	l-olefin/l-paraffin
36	Recycle Stream	Mainly methyl-branched paraffins	b-paraffin
37	Hydrocarbon Feed	F.T. gasoline, higher cuts; crackate from slack wax; crackate from Flexicoker or Fluidcoker	b-olefin/l-olefin/ b-paraffin/l-paraffin
38	Branched-enriched Stream (Intermediate)	Branched olefins, branched paraffins, cyclics and aromatics	b-olefin/b-paraffin
39	Branched-enriched Stream	Mainly methyl branched olefins and methyl branched paraffins; variable ratio	b-olefin/b-paraffin
40	Branched-enriched Stream (Olefinic)	Mainly methyl branched paraffins; methyl branched olefins must be present, e.g., at up to about 20%	b-paraffin/b-olefin
41	Modified Alkylbenzene	Mainly methyl-branched alkylbenzenes	Modified Alkylbenzenes produced by FIG. 6 process
42	Linear-enriched Stream	Mainly linear olefins and linear paraffins	l-olefin/l-paraffin
43	Reject Stream (Cyclics/ Aromatics)	Cyclics, aromatics, ethyl- and higher branched hydrocarbons	
44	Recycle Stream	Mainly methyl-branched paraffins	b-paraffin
45	Hydrocarbon Feed	F.T. gasoline, higher cuts; crackate from slack wax; crackate from Flexicoker or Fluidcoker	b-olefin/l-olefin/ b-paraffin/l-paraffin
46	Branched-enriched Stream	Mainly methyl-branched and linear olefins; usually have some linear and methyl branched paraffins	b-olefin/l-olefin/ b-paraffin/l-paraffin
47	Branched-enriched Stream (Olefinic)	Mainly linear and methyl-branched paraffins; will have some linear and methyl branched olefins	b-paraffin/l-paraffin/ b-olefin/l-olefin
48	Modified Alkylbenzene	Mainly methyl-branched and linear alkylbenzenes	Modified Alkylbenzenes produced by FIG. 7 process
49	Reject Stream (Cyclics/ Aromatics)	Cyclics, aromatics, ethyl- and higher branched hydrocarbons	
50	Recycle Stream	Mainly methyl-branched and linear paraffins	b-paraffin l-paraffin
51	Crude hydrocarbon feed	Kerosene-range paraffins; 360–500° F. (182–277° C.) preferably from light paraffinic crudes.	b-paraffin l-paraffin

-continued

Stream	Stream Type/ Name	Exemplary Sources (for Feeds) or compositions (for streams)	Predominant Component(s)
52	Light distillation cuts (not used for making OXO alcohol or modified LAB)	Light cuts - e.g., 360° F. to product cut.	
54	Branched-enriched stream (Olefinic) (De-diolefinized)	Mainly methyl-branched paraffins and methyl-branched olefins will be present e.g., up to about 20% (essentially free of diolefins and/or aromatics)	b-paraffins b-olefins
55	Branched-enriched stream (Olefinic) (De-paraffinized)	Mainly methyl-branched olefins	b-olefins
56	Modified primary OXO alcohols	Mainly modified primary OXO alcohols plus trace paraffins	modified primary OXO alcohols
57	Modified primary OXO alcohols (freed from recyclable materials)	Modified primary OXO alcohols alcohols	modified primary OXO
58	Crude modified primary OXO alcohols	Mainly modified primary OXO alcohols plus some alpha-, omega- diols, plus trace paraffins	modified primary OXO alcohols
59	modified alkylbenzenes plus paraffins	Mainly methyl-branched paraffins plus up to 30% modified alkylbenzenes	b-paraffins modified alkylbenzenes
60	Modified primary OXO alcohols plus paraffins	Mainly methyl-branched paraffins plus up to about 25% modified primary OXO alcohols	b-paraffin modified primary OXO alcohols
61	linear plus methyl-branched olefins in paraffins	Mainly linear paraffins and methyl-branched paraffins, linear olefins and methyl-branched olefins will be present, e.g., at up to about 20% (essentially free of diolefins and/or aromatics) (The linear compounds effectively "dilute" the branched)	b-paraffins l-paraffins b-olefins l-olefins
62	linear and methyl-branched olefins	Mainly linear olefins and methyl-branched olefins	b-olefins l-olefins
63	mixture of modified primary OXO alcohols and conventional OXO alcohols	Mainly conventional OXO alcohols and modified primary OXO alcohols, plus trace paraffins	modified primary OXO alcohols linear OXO alcohols
64	another mixture of modified primary OXO alcohols and conventional OXO alcohols	Mainly conventional OXO alcohols and modified primary OXO alcohols, without trace paraffins	modified primary OXO alcohols linear OXO alcohols
65	mixture in paraffins of modified primary OXO alcohols and conventional OXO alcohols	Mainly linear paraffins and methyl-branched paraffins plus up to about 25% conventional OXO alcohols (the primary OXO alcohol type formed from OXO reaction on a linear feedstock) and modified primary OXO alcohols	b-paraffins l-paraffins modified primary OXO alcohols linear OXO alcohols
66	mixture in paraffins of mixtures of modified alkylbenzenes and linear alkylbenzenes	Mainly linear paraffins and methyl-branched paraffins plus up to about 30% linear alkylbenzenes and modified alkylbenzenes	b-paraffins l-paraffins modified alkylbenzenes l-alkylbenzenes

The hydrocarbon feeds exemplified in the table hereinabove should of course be viewed as illustrative and not limiting of the present invention Any other suitable hydrocarbon feed may be used. For example, crackates of petroleum waxes including crackates of Fischer-Tropsch waxes. These waxes are from lube oil distillate fractions and melt in the relatively low range up to about 72° C., e.g., in the range from about 50° C. to about 70° C. and contain from about 18 to about 36 carbon atoms. Such waxes preferably contain 50% to 90% normal alkanes and 10% to 50% of monomethyl branched alkanes and low levels of various cyclic alkanes. Such crackate feeds are especially useful in alternate embodiments of the invention as further described in detail hereinafter, and are described in "Chemical Economics Handbook", published by SRI, Menlo Park, Calif. See, for example "Waxes", S95.5003 L, published 1995 Paraffin waxes are also described in Kirk Othmer's Encyclopedia of Chemical Technology, 3^{rd} Edition, (1984), Volume 24. See "Waxes" at page 473. Any equivalent alternative hydrocarbon feeds or more preferably shorter-chain equivalents in the C10–C20 range and having appreciable monomethyl-branching in any position on the chain, for example from Fischer-Tropsch synthesis, are also suitable.

Hydrocarbon feeds herein can contain varying amounts of N,O,S impurity. Certain preferred hydrocarbon feeds, especially if derived from sulfur- and/or nitrogen-containing fractions, are desulfurized and/or freed from nitrogenous matter using conventional desulfurization or "de-NOS' technology.

Hydrocarbon feeds herein can be separated before use in the present processes so that the maximum amount of hydrocarbons having specific chainlengths and/or degrees of branching are most effectively utilized to make modified alkylbenzenes and/or modified primary OXO alcohols. For example, though not specifically illustrated in the Figures, it may be desirable to use two paraffin cuts from kerosene for two essentially parallel processes, each as described herein, one including an alkylation stage to form modified alkylbenzene, and one including an OXO stage to form modified primary OXO alcohols. In such a dual process, it might typically be preferred to use a cut having overall lower carbon number for the modified alkylbenzene manufacturing (for example a cut rich in C11–C13 hydrocarbons), while a heavier cut, for example one richer in C14–C17 hydrocarbons might be used for making modified OXO alcohols. Other process permutations include using multiple hydrocarbon streams or cuts for concurrently manufacturing both modified and non-modified (conventional) alkylbenzenes and/or OXO alcohols.

Adsorptive Separation Step(s)

In general, separation techniques in stage (a) or stage (A) of the instant processes rely on adsorption on porous media and/or use of clathrates. A landmark patent on adsorptive separation is U.S. Pat. No. 2,995,589 which illustrates devices, adsorbent beds and process conditions of temperature and pressure generally suitable for use herein. '589 does not describe critical modifications, especially pore sizes for specific separations and connection of steps, that are part of the present invention.

Adsorptive separation steps herein can, in general, be conducted in the vapor phase or the liquid phase, and may or may not employ any of the commercialized process equipment as identified in the background of the invention.

Porous media used as adsorbents can in general be dried or non-dried. Preferred embodiments include those wherein the adsorbents are dried and contain less than about 2% free moisture.

Any adsorptive separation step according to the present invention may, or may not use a desorbent or displacing agent. In general, any desorption means, such as pressure-swing or other means, can be used. However, preferably such desorbing agent is used, in other words, solvent displacement is a preferred method of desorbing streams from the porous media used herein. Suitable desorbents or displacing agents include a lower-molecular weight n-paraffin such as heptane, octane or the like, or a polar desorbent such as ammonia. It should be understood that, irrespective of their presence, such well-known desorbents, being fully conventional, are not explicitly included in identifying any of the streams or their compositions in the processes herein, and can be recycled at will using desorbent recycle steps not explicity shown in FIGS. **1**–**18**.

In the present process, stage (a) can use a MOLEX® process step of UOP, subject to the difference that the present process must have at least one adsorptive separation using a porous material which has larger pores than the usual 5 Angstrom zeolite as used in linear alkylbenzene manufacture. MOLEX® is discussed in the hereinabove-identified Surfactant Science Series Vol. 56, including for example pages 5–10. Vapor-phase processes such as Union Carbide's IsoSiv process (see the same reference) are also useful but less preferred.

Apparatus and operating conditions for the MOLEX® process in any version used herein are well-known, see, for example the above-identified reference at page 9 showing the process and its various streams including raffinate and absorbent in detail.

Porous Media (Larger-pore Types)

Porous media required in stage (a) or stage (A) herein are larger-pore types. By "larger-pore" is specifically meant porous media having pores large enough to retain mono-methyl-branched linear olefinic or paraffinic hydrocarbons and dimethyl-branched or trimethyl-branched linear olefinic or paraffinic hydrocarbons other than gem-dimethyl hydrocarbons, while being small enough to at least partly exclude gem-dimethyl, ethyl and higher-branched hydrocarbons as well as cyclic (e.g., 5-, 6-membered rings) and aromatic hydrocarbons. Such pore sizes large enough to retain appreciable amounts of methyl-branched hydrocarbons are invariably not used in conventional linear alkylbenzene manufacture and in general are far more rarely used in any commercial processes than are the more familiar 4–5 Angstrom pore size zeolites. The larger-pore porous media are those used in FIGS. **1**–**7** in the adsorptive separation units marked as "SOR 5/7".

Porous media essential in stage (a) or stage (A) herein accordingly have a minimum pore size larger than the pore size required for selective adsorption of linear acyclic hydrocarbons, i.e., in excess of those used in conventional linear alkylbenzene manufacture, said pore size not exceeding about 20 Angstroms, more preferably not exceeding about 10 Angstroms and very preferably, from above about S Angstroms to about 7 Angstroms on average. When specifying minimum pore size for the so-called "larger-pore" porous materials herein, it should be recognized that such materials often have elliptical pores, for example SAPO-11 has a pore size of 4.4 by 6.7 Angstrom. (5.55 Angstrom average). See S. Miller, Microporous Materials, Vol. 2., pages 439–449 (1994). When comparing such a material with a "smaller-pore" zeolite such as a 4–5 Angstrom uniform-pore zeolite, the convention herein is to look to the average of elliptical dimensions or the larger elliptical dimension—in any event not to the smaller elliptical dimension—when making the size comparison. Thus the SAPO-11 material herein by definition has a pore size larger than a 5 Angstrom, uniform-pore zeolite.

Porous media having the larger pores essential in stage (a) or stage (A) herein can be either zeolites (aluminosilicates) or non-zeolites.

Suitable non-zeolites include the silicoaluminophosphates, especially SAPO-11 though other silicoaluminophosphates, e.g., SAPO 31 or 41, can be used if the average pore size is greater than about 5 Angstroms or if elliptical pores are present with at least one elliptical dimension above 5 Angstroms.

Another technique suitable for adsorptive separation herein is sorption using pyrolyzed poly(vinylidene chloride) i.e., pyrolyzed SARAN, for example manufactured according to Netherlands Application NL 7111508 published Oct. 25, 1971. Preferred materials have sieve diameter of from 4–7 Angstrom. When using such material as the essential adsorbent, a pore size above about 5 Angstrom will be used.

Use of Organometallic-grafted Mordenites and other grafted zeolites as Porous Media in Stage (a) or Stage (A)

The present invention also includes especially useful embodiments wherein the adsorptive separations of stage (a) or stage (A) comprise at least one separation step using an organometallic-grafted mordenite. Especially suitable as the "large-pore" porous media herein are grafted mordenites such as a tin-grafted mordenite. Likewise, and more generally, the invention encompasses a method comprising use of a grafted mordenite for manufacturing detergent surfactants and any of the corresponding surfactants and consumer products produced by use of these specific porous media in any of the above-defined processes. See EP 559,510 A Aug. 18, 1993 incorporated by reference in its entirety. The practitioner will select those grafted mordenites of EP 559,510 which are clearly identifiable from the Examples thereof to be best suited for separations of linear and monomethyl-branched hydrocarbons from gem-dimethyl and polymethyl hydrocarbons.

Other grafted zeolites useful as the porous media herein include those of U.S. Pat. No. 5,326,928, also incorporated by reference in its entirety. In such embodiments of the instant invention, it is especially preferred to integrate into a single process the use both of the above-identified grafted mordenite in stage (a), and the use of an at least partially dealuminized H-mordenite in step (c), the alkylation step defined elsewhere herein.

On this basis, using the terminology of U.S. Pat. No. 5,326,928 to describe the process module containing the grafted component and combining therewith the preferred alkylation step as defined herein, the present invention also encompasses a process for making modified alkylbenzenes and/or modified alkylbenzenesulfonates, said process comprising: (a) at least one stage of separating aliphatic paraffins having varying degrees of branching in a hydrocarbon charge containing molecules of 9 to 14 carbon atoms into at least one 1o first effluent comprising less branched (linear and monomethyl, optionally some dimethyl-branched) paraffins and at least one second effluent comprising more branched paraffins (trimethyl and higher-branched paraffins and optionally cyclic and/or aromatic impurities), said separation comprising contacting the hydrocarbon charge with at least one adsorbent bed comprising at least one microporous solid (as defined in U.S. Pat. No. 5,326,928) having grafted in the pores thereof an organometallic compound of a quantity and shape sufficient to yield pores selective for entry of the less branched paraffins but not the more branched paraffins; (b) at least one stage of alkylating a less branched effluent of stage (a), preferably in an alkylation having internal isomer selectivity of from 0 to 40, and more preferably still, using an at least partially dealuminized, at least partially acidic H-mordenite as catalyst; and (c) at least one stage of sulfonating the product of stage (b) using any conventional sulfonating agent. The resulting modified alkylbenzenesulfonic acid can be neutralized and incorporated into cleaning products as taught elsewhere herein.

In stage (a) or stage (A) of the present process, there is a preference to use zeolites or other porous media in such a form that they do not actively promote chemical reactions of the feedstock., e.g., cracking, polymerization. Thus, acidic mordenite is preferably avoided in stage (a) or stage (A). See in contrast alkylation catalysts hereinafter, in which at least partial acid-form is preferred.

Porous Media (Smaller-pore Types)

Smaller-pore zeolites optionally useful in stage (a) or stage (A) herein, for example 30 those used in processes such as those of the adsorptive separation unit identified as "SOR 4/5" in FIGS. **1**, **2**, **5**, **6**, **9**, etc. are those which selectively adsorb linear hydrocarbons and which do not adsorb methyl-branched hydrocarbons appreciably. Such porous materials are well-known and include, for example, Calcium Zeolites with 4–5 Angstrom pores. Such materials are further illustrated in U.S. Pat. No. 2,985,589 and are those in current commercial use for manufacture of linear alkylbenzenes.

Porous Media (e.g., OLEX® or Similar Processes)

When making modified primary OXO alcohols herein, it may be desirable to conduct an olefin/paraffin separation step in stage (C) to concentrate mono-olefins. See "SOR O/P" in the Figures and stage (C) in the claims. Suitable porous media for this stage include copper- or silver-treated zeolite X or zeolite Y. See, for example, U.S. Pat. No. 5,300,715 or U.S. Pat. No. 4,133,842, and references cited therein. See also U.S. Pat. No. 4,036,744 and U.S. Pat. No. 4,048,111. Alternatively, UOP Corp., a technology licenser, has an entire process known as OLEX® available for license.

Clathration

Urea clathration can also be used herein in stage (a) for separating n-paraffins from branched paraffins, as is well known in the art. See, for example, Surfactant Science Series, Marcel Dekker, N.Y., 1996, Vol. 56, pages 9–10 and references therein. See also "Detergent Manufacture Including Zeolite Builders and other New Materials, Ed. Sittig., Noyes Data Corp., 1979, paces 25–30 and especially U.S. Pat. No. 3,506,569 incorporated in its entirety which uses solid urea and no chlorocarbon solvents. More generally but less preferably, processes according to U.S. Pat. No. 3,162,627 may be used.

Dehydrogenation

In general, dehydrogenation of the olefin or olefin/paraffin mixtures in the instant process can be accomplished using any of the well-known dehydrogenation catalyst systems, including those described in the Surfactant Science Series references cited in the background as well as in "Detergent Manufacture Including Zeolite Builders and Other New Materials", Ed. Sittig, Noyes Data Corp., New Jersey, 1979 and other dehydrogenation catalyst systems, for example those commercially available though UOP Corp. Dehydrogenation can be conducted in presence of hydrogen gas and commonly a precious metal catalyst (e.g., DeH-5®, DeH-7®, DeH-9® available from UOP) is present though alternatively non-hydrogen, precious-metal free dehydrogenation systems such as a zeolite/air system can be used with no precious metals present.

More specifically, dehydrogenation catalysts useful herein include a catalyst supported on Sn-containing alumina and having Pt: 0.16%, Ir: 0.24%, Sn: 0.50%, and Li: 0.54% as described in U.S. Pat. No. 5,012,027 incorporated by reference. This catalyst, when contacted with a C9–C14 paraffin mixture (believed to be linear) at 500° C. and 0.68 atm. produces olefinic products (38 h on stream) with 90.88% selectivity and 11.02% conversion and is believed to be very suitable for at least partially dehydrogenating branched-enriched streams of paraffins herein. See also U.S. Pat. No. 4,786,625; EP 320,549 A1 Jun. 21, 1989; Vora et al., Chem. Age, India (1986), 37(6), 415–18;

As noted supra, dehydrogenation can be complete or partial, more typically partial. When partial, this step forms a mixture of olefin (e.g., about 10% though this figure is illustrative and should not be taken as limiting) and the balance unreacted paraffin. Such mixture is a suitable feed for the alkylation step of the instant process.

Other useful dehydrogenation systems readily adapted into the present invention include those of U.S. Pat. No. 4,762,960 incorporated by reference which discloses a Pt-group metal containing dehydrogenation catalyst having a modifier metal selected from the group consisting of Sn, Ge, Re and their mixtures, an alkali metal, an alkaline earth metal or their mixtures, and a particularly defined refractory oxide support.

Alternative dehydrogenation catalysts and conditions useful herein include those of U.S. Pat. No. 4.886,926 and of U.S. Pat. No. 5,536,695.

Alkylation

Important embodiments of the present invention further include alkylation, which takes place after delinearization by separative enrichment of lightly branched paraffin and at least partial dehydrogenation of the delinearized olefin or olefin/paraffin mixtures. Alkylation is conducted with an aromatic hydrocarbon selected from benzene, toluene and mixtures thereof

Internal Isomer Selectivity and Selection of Alkylation Step

Preferred embodiments of the present processes require an alkylation step having internal isomer selectivity in the range from 0 to 40, preferably from 0 to 20, more preferably still from 0 to 10. The Internal Isomer Selectivity or "IIS" as defined herein is measured for any given alkylation process step by conducting a test alkylation of benzene by 1-dodecene at a molar ratio of 10:1. The alkylation is conducted in the presence of an alkylation catalyst to a conversion of dodecene of at least 90% and formation of monophenyldodecanes of at least 60%. Internal isomer selectivity is then determined as:

$$IIS = 100 * \left(1 - \frac{\text{amount of terminal phenyldodecanes}}{\text{amount of total phenyldodecanes}}\right)$$

wherein amounts are amounts of the products by weight, the amount of terminal phenyldodecanes is the amount of the sum of 2-phenyldodecane and 3-phenyldodecane and the amount of total phenyldodecanes is the amount of the sum of 2-phenyldodecane and 3-phenyldodecane and 4-phenyldodecane and 5-phenyldodecane and 6-phenyldodecane and wherein said amounts are determined by any known analytical technique for alkylbenzenesulfonates such as gas chromatography. See Analytical Chemistry, Nov. 1983, 55 (13), 2120–2126, Eganhouse et al, "Determination of long-chain alkylbenzenes in environmental samples by argentation thin-layer chromatography—high resolution gas chromatography and gas chromatography/mass spectrometry". In computing IIS according to the above formula, the amounts are divided before subtracting the result from 1 and multiplying by 100. It should of course be understood that the specific alkenes used to characterize or test any given alkylation step for suitability are reference materials permitting a comparison of the alkylation step herein with known alkylation steps as used in making linear alkylbenzenes and permitting the practitioner of the invention to decide if a given known alkylation step is, or is not, useful in the context of the series of process steps constituting the present invention. In the process of the invention as practiced, the hydrocarbon feedstock for alkylation actually used is of course that which is specified on the basis of the preceding process steps. Also to be noted, all the current commercial processes for LAS manufacture are excluded from preferred embodiments of the present invention solely on the basis of the IIS for the alkylation step. For example, LAS processes based on aluminum chloride, HF and the like all have IIS outside of the range specified for the instant process. In contrast, a few alkylation steps described in the literature but not currently applied in commercial alkylbenzenesulfonate production do have suitable IIS and are useful herein.

The better to assist the practitioner in determining IIS and in deciding whether a given alkylation process step is suitable for the purposes of the present invention, the following are more particular examples of ITS determination.

As noted, test alkylation of benzene by 1-dodecene is conducted at a mole ratio of 10:1 benzene to 1-dodecene and the alkylation is conducted in the presence of an alkylation catalyst to a conversion of dodecene of at least 90% and formation of monophenyldodecanes of at least 60%. The alkylation test must in general be conducted in a reaction time of less than 200 hours and at a reaction temperature of from about −15° C. to about 500° C., preferably from about 20° C. to 500° C. Pressure and catalyst concentration relative to 1-dodecene can vary widely. No solvent other than benzene is used in the test alkylation. The process conditions used to determine the IIS for the catalyst or alkylation step in question can be based on the literature. The practitioner will use generally appropriate conditions based on a large body of well-documented data for alkylations. For example, appropriate process conditions o determine if an $AlCl_3$ alkylation can be used herein are exemplified by a reaction of 5 mole % $AlCl_3$ relative to 1-dodecene at 20–40° C. for 0.5–1.0 hour in a batch reactor. Such a test demonstrates that an $AlCl_3$ alkylation step is unsuitable for use in the present process. An IIS of about 48 should be obtained. In another example, an appropriate test of alkylation using HF as a catalyst should give an IIS of about 60. Thus, neither $AlCl_3$ alkylation nor HF alkylation is within the scope of this invention. For a medium-pore zeolite such as a dealuminized mordenite, process conditions suitable for determining ITS are exemplified by passing 1-dodecene and benzene at a mole ratio of 10:1 across the mordenite catalyst at a WHSV of 30 Hr^{-1} at a reaction temperature of about 200° C. and a pressure of about 200 psig which should give an IIS of about 0 for the mordenite catalyst. The temperatures and pressures for the exemplary mordenite alkylation test (see also the detailed examples of the instant process hereinafter) are expected to be more generally useful for testing zeolites and other shape-selective alkylation catalysts. Using a catalyst such as H-ZSMA-4 one should obtain an IIS of about 18. Clearly both the dealuminized mordenite and H-ZSM-4 catalyzed alkylations give acceptable IIS for the invention, with the mordenite being superior.

Without intending to be limited by theory, it is believed that the low-IIS alkylation step practiced using H-mordenites herein is capable both of alkylating benzene with the branched-enriched hydrocarbon, but very usefully also of scrambling the position of a methyl branch attached to the hydrocarbon chain.

Alkylation Catalyst

Accomplishing the required IIS in the alkylation process step is made possible by a tightly controlled selection of alkylation catalysts. Numerous alkylation catalysts are readily determined to be unsuitable. Unsuitable alkylation catalysts include the DETAL® process catalysts, aluminum chloride, HF, HF on zeolites, fluoridated zeolites, non-acidic calcium mordenite, and many others. Indeed no alkylation catalyst currently used for alkylation in the commercial production of detergent linear alkylbenzenesulfonates has yet been found suitable

In contrast, suitable alkylation catalyst herein is selected from shape-selective moderately acidic alkylation catalysts, preferably zeolitic. The zeolite in such catalysts for the alkylation step (step (b)) is preferably selected from the group consisting of mordenite, ZSM4, ZSM-12, ZSM-20, offretite, gmelinite and zeolite beta in at least partially acidic form. More preferably, the zeolite in step (b) (the alkylation step) is substantially in acid form and is contained in a catalyst pellet comprising a conventional binder and further wherein said catalyst pellet comprises at least about 1%, more preferably at least 5%, more typically from 50% to about 90%, of said zeolite.

More generally, suitable alkylation catalyst is typically at least partially crystalline, more preferably substantially crystalline not including binders or other materials used to form catalyst pellets, aggregates or composites. Moreover the catalyst is typically at least partially acidic. Fully exchanged Ca-form mordenite, for example, is unsuitable whereas H-form mordenite is suitable. This catalyst is useful for the alkylation step identified as step (b) in the claims hereinafter: these correspond to Step 7 in FIG. **1**.

The pores characterizing the zeolites useful in the present alkylation process may be substantially circular, such as in cancrinite which has uniform pores of about 6.2 angstroms, or preferably may be somewhat elliptical, such as in mordenite. It should be understood that, in any case, the zeolites used as catalysts in the alkylation step of the present process have a major pore dimension intermediate between that of the large pore zeolites, such as the X and Y zeolites, and the relatively small pore size zeolites ZSM-5 and ZSM-11, and preferably between about 6A and about 7A. Indeed ZSM-5 has been tried and found inoperable in the present invention. The pore size dimensions and crystal structures of certain zeolites are specified in ATLAS OF ZEOLITE STRUCTURE TYPES by W. M. Meier and D. H. Olson, published by the Structure Commission of the International Zeolite Association (1978 and more recent editions) and distributed by Polycrystal Book Service, Pittsburgh, Pa.

The zeolites useful in the alkylation step of the instant process generally have at least 10 percent of the cationic sites thereof occupied by ions other than alkali or alkaline-earth metals. Typical but non-limiting replacing ions include ammonium, hydrogen, rare earth, zinc, copper and aluminum Of this group, particular preference is accorded ammonium, hydrogen, rare earth or combinations thereof in a preferred embodiment, the zeolites are converted to the predominantly hydrogen form, generally by replacement of the alkali metal or other ion originally present with hydrogen ion precursors, e.g., ammonium ions, which upon calcination yield the hydrogen form. This exchange is conveniently carried out by contact of the zeolite with an ammonium salt solution, e.g., ammonium chloride, utilizing well known ion exchange techniques. In certain preferred embodiments, the extent of replacement is such as to produce a zeolite material in which at least 50 percent of the cationic sites are occupied by hydrogen ions.

The zeolites may be subjected to various chemical treatments, including alumina extraction (dealumination) and combination with one or more metal components, particularly the metals of Groups IIB, III, IV, VI, VII and VIII. It is also contemplated that the zeolites may, in some instances, desirably be subjected to thermal treatment, including steaming or calcination in air, hydrogen or an inert gas. e.g. nitrogen or helium.

A suitable modifying treatment entails steaming of the zeolite by contact with an atmosphere containing from about 5 to about 100 percent steam at a temperature of from about 250° C. to 1000° C. Steaming may last for a period of between about 0.25 and about 100 hours and may be conducted at pressures ranging from sub-atmospheric to several hundred atmospheres.

In practicing the desired alkylation step of the instant process, it may be useful to incorporate the above-described intermediate pore size crystalline zeolites in another material, e.g., a binder or matrix resistant to the temperature and other conditions employed in the process. Such matrix materials include synthetic or naturally occurring substances as well as inorganic materials such as clay, silica, and/or metal oxides. Matrix materials can be in the form of gels including mixtures of silica and metal oxides. The latter may be either naturally occurring or in the form of gels or gelatinous precipitates. Naturally occurring clays which can be composited with the zeolite include those of the montmorillonite and kaolin families, which Families include the sub-bentonites and the kaolins commonly known as Dixie, McNamee-Georgia and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite or anauxite. Such clays can be used in the raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification.

In addition to the foregoing materials, the intermediate pore size zeolites employed herein may be compounded with a porous matrix material, such as alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, and silica-titania, as well as ternary combinations, such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia The matrix may be in the form of a cogel. The relative proportions of finely divided zeolite and inorganic oxide gel matrix may vary widely, with the zeolite content ranging from between about 1 to about 99 percent by weight and more usually in the range of about 5 to about 80 percent by weight of the composite.

A group of zeolites which includes some useful for the alkylation step herein have a silica:alumina ratio of at least 10:1, preferably at least 20:1. The silica:alumina ratios referred to in this specification are the structural or framework ratios, that is, the ratio for the SiO4 to the AlO4 tetrahedra. This ratio may vary from the silica:alumina ratio determined by various physical and chemical methods. For example, a gross chemical analysis may include aluminum which is present in the form of cations associated with the acidic sites on the zeolite, thereby giving a low silica:alumina ratio. Similarly, if the ratio is determined by thermogravimetric analysis (TGA) of ammonia desorption, a low ammonia titration may be obtained if cationic aluminum prevents exchange of the ammonium ions onto the acidic sites. These disparities are particularly troublesome when certain treatments such as the dealumination methods described below which result in the presence of ionic aluminum free of the zeolite structure are employed. Due care should therefore be taken to ensure that the framework silica:alumina ratio is correctly determined.

Zeolite beta suitable for use herein (but less preferred than H-mordenite) is disclosed in U.S. Pat. No. 3,308,069 to which reference is made for details of this zeolite and its preparation. Such a zeolite in the acid form is also commercially available as Zeocat PB/H from Zeochem.

When the zeolites have been prepared in the presence of organic cations they are catalytically inactive, possibly because the intracrystalline free space is occupied by organic cations from the forming solution. They may be activated by heating in an inert atmosphere at 540° C. for one hour, for example, followed by base exchange with ammonium salts followed by calcination at 540° C. in air The presence of organic cations in the forming solution may not be absolutely essential to the formation of the zeolite; but it does appear to favor the formation of this special type of zeolite. Some natural zeolites may sometimes be converted to zeolites of the desired type by various activation procedures and other treatments such as base exchange, steaming, alumina extraction and calcination. The zeolites preferably have a crystal framework density, in the dry hydrogen form, not substantially below about 1.6 g.cm −3. The dry density for known structures may be calculated from the number of silicon plus aluminum atoms per 1000 cubic Angstroms, as given, e.g., on page 19 of the article on Zeolite Structure by W M. Meier included in "Proceedings of the Conference on Molecular Sieves, London, April 1967", published by the Society of Chemical industry, London, 1968. Reference is made to this paper for a discussion of the crystal framework density. A further discussion of crystal framework density, together with values for some typical zeolites, is given in U.S. Pat. No. 4,016,218, to which reference is made. When synthesized in the alkali metal form, the zeolite is conveniently converted to the hydrogen form, generally by intermediate formation of the ammonium form as a result of ammonium ion exchange and calcination of the ammonium form to yield the hydrogen form. It has been found that although the hydrogen form of the zeolite catalyzes the reaction successfully, the zeolite may also be partly in the alkali metal form.

EP 466,558 describes an acidic mordenite type alkylation catalyst also of possible use herein having overall Si/Al atomic ratio of 15–85 (15–60), Na weight content of less than 1000 ppm (preferably less than 250 ppm), having low or zero content of extra-network Al species, and an elementary mesh volume below 2,760 nm3.

U.S. Pat. No. 5,057,472 useful for preparing alkylation catalysts herein relates to concurrent dealumination and ion-exchange of an acid-stable Na ion-containing zeolite, preferably mordenite effected by contact with a 0.5–3 (preferably 1–2.5) M HNO3 solution containing sufficient NH4NO3 to fully exchange the Na ions for NH4 and H ions. The resulting zeolites can have an SiO2:Al2O3 ratio of 15–26 (preferably 17–23):1 and are preferably calcined to at least partially convert the NH4/H form to an H form. Optionally, though not necessarily particularly desirable in the present invention, the catalyst can contain a Group VIII metal (and optionally also an inorganic oxide) together with the calcined zeolite of '472.

Another acidic mordenite catalyst useful for the alkylation step herein is disclosed in U.S. Pat. No. 4,861,935 which relates to a hydrogen form mordenite incorporated with alumina, the composition having a surface area of at least 580 m2/g Other acidic mordenite catalysts useful for the alkylation step herein include those described in U.S. Pat. No. 5.243,116 and U.S. Pat. No. 5,198,595. Yet another alkylation catalyst useful herein is described in U.S. Pat. No. 5,175,135 which is an acid mordenite zeolite having a silica/alumina molar ratio of at least 50:1, a Symmetry Index of at least 1.0 as determined by X-ray diffraction analysis, and a porosity such that the total pore volume is in the range from about 0.18 cc/g to about 0.45 cc/g and the ratio of the combined meso- and macropore volume to the total pore volume is from about 0.25 to about 0.75.

Particularly preferred alkylation catalysts herein include the acidic mordenite catalysts Zeocat™ FM-8/25H available from Zcochem, CBV 90 A available from Zeolyst International, and LZM-8 available from UOP Chemical Catalysts.

Most generally, any alkylation catalyst may be used herein provided that the alkylation step meets the internal isomer selectivity requirements identified supra.

Most generally, any alkylation catalyst may be used herein provided that the alkylation step meets the internal isomer selectivity requirements identified supra

Distillation of Modified Alkylbenzenes or Modified Primary OXO Alcohols

Optionally, depending on feedstock and the precise sequence of steps used, the present process can include distillation of modified alkylbenzenes or modified primary OXO alcohols, for example to remove unreacted starting materials, paraffins, excesses of benzene and the like Any conventional distillation apparatus can be used The general practice is similar to that used for distillation of commercial linear alkylbenzenes (LAB) or OXO alcohols. Suitable distillation steps are described in the hereinabove-referenced Surfactant Science Series, e.g., the review of alkylbenzenesulfonate manufacture.

Sulfonation/Sulfation and Workup

In general, sulfonation of the modified alkylbenzenes or sulfation of modified primary OXO alcohols (or their alkoxylates) in the instant process can be accomplished using any of the well-known sulfonation systems, including those described in the hereinabove-referenced volume "Detergent Manufacture Including Zeolite Builders and Other New Materials" as well as in the hereinabove-referenced Surfactant Science Series review of alkylbenzenesulfonate manufacture. Common sulfonation systems include sulfuric acid, chlorosulfonic acid, oleum, sulfur trioxide and the like. Sulfur trioxide/air is especially preferred. Details of sulfonation using a suitable air/sulfur trioxide mixture are provided in U.S. Pat. No. 3,427,342, Chemithon. Sulfonation processes are further extensively described in "Sulfonation Technology in the Detergent Industry", W. H. de Groot, Kiuwer Academic Publishers, Boston, 1991

Any convenient workup steps may be used in the present process. Common practice is to neutralize after sulfonation with any suitable alkali Thus the neutralization step can be conducted using alkali selected from sodium, potassium, ammonium, magnesium and substituted ammonium alkalis and mixtures thereof. Potassium can assist solubility, magnesium can promote soft water performance and substituted ammonium can be helpful for formulating specialty variations of the instant surfactants. The invention encompasses any of these derivative forms of the modified alkylbenzenesulfonate surfactants, or of the sulfated modified primary OXO alcohols, or of the alkoxylated, sulfated modified primary OXO alcohols as produced by the present process and their use in consumer product compositions.

Alternately the acid form of the present surfactants can be added directly to acidic cleaning products, or can be mixed with cleaning ingredients and then neutralized.

Post-alkylation Steps

As noted, the modified alkylbenzene manufacturing process herein includes embodiments having steps that take place subsequent to the alkylation step (c). These steps preferably include (d) sulfonating the product of step (c); and one or more steps selected from (e) neutralizing the product of step (d), and (f) mixing the product of step (d) or (e) with one or more cleaning product adjunct materials; thereby forming a cleaning product.

Blended Embodiments

In one preferred embodiment, prior to said sulfonation step, modified alkylbenzene which is the product of said step (c) is blended with a linear alkylbenzene produced by a conventional process. In another such embodiment, in any step subsequent to said sulfonation step, modified alkylbenzene sulfonate which is the product of said step (d) is blended with a linear alkylbenzene produced by a conventional process. In these blended embodiments, a preferred process has a ratio of modified alkylbenzene to linear alkylbenzene of from about 10:90 to about 50:50. Corresponding blending schemes are of course likewise applicable to modified primary OXO alcohol processes herein. Moreover, any blends can be made of the different types of surfactant, or their precursors, herein. For example, the practitioner can freely blend modified alkylbenzene with modified primary OXO alcohol as made herein, alkoxylate the mixture using ethylene oxide, propylene oxide, etc., and then sulfate/sulfonate the resulting mixture. Moreover, since in general, modified OXO alcohols can be separated by distillation and various other OXO alcohols including linear OXO alcohol types are known from the art, the present invention also includes processes of blending any of the modified or branched OXO alcohols attainable herein with any known linear OXO alcohol in any proportion, such as from about 1:100 to about 100:1 by weight branched:linear OXO alcohol, and of converting any of such OXO alcohol blends to surfactants useful for detergents.

Other Process Embodiments

The present invention also encompasses a process for beneficiating an effluent stream from the manufacture of linear alkylbenzenesulfonate surfactants useful in cleaning products, said process comprising (i) at least partially separating an isoparaffin into a normal paraffin enriched stream and an effluent stream having the form of an isoparaffin (especially methyl branched paraffin) enriched stream comprising at least about 10% isoparaffin and having molecular weight of at least about 128 and no more than about 282 wherein said separation comprises at least one step selected from clathration by means of urea and separation by means of sorption and wherein said steps are integral in a process for linear alkylbenzene manufacture; (ii) at least partially further enriching the isoparaffin content of said effluent stream by at least one step selected from urea clathration and adsorptive separation; wherein said step is additional to and follows step (i); and (iii) a step of at least partially dehydrogenating the isoparaffin enriched stream of said step (ii).

More generally, it is contemplated that the hydrocarbons produced herein can be useful not only in modified alkylbenzenesulfonate surfactants as nonlimitingly illustrated herein but also in modified surfactants other than alkylbenzenesulfonates (such as alkyl sulfates). Thus the present invention also encompasses a process for beneficiating a branched paraffinic effluent stream comprising (i) at least partially separating an isoparaffin into a normal paraffin enriched stream and an effluent stream having the form of an isoparaffin enriched stream comprising, at least about 10% isoparaffin wherein said separation comprises at least one step selected from clathration by means of urea and separation by means of sorption; (ii) at least partially further enriching the isoparaffin content of said effluent stream by at least one step selected from urea clathration and adsorptive separation; wherein said step is additional to and follows step (i); and (iii) a step of at least partially dehydrogenating the isoparaffin enriched stream of said step (ii).

In such embodiments, the isoparaffin enriched stream may vary from about C10 to about C20 in overall carbon content and the nonlinear fraction of said enriched stream comprises an average of from about one to about two methyl side chains other than terminal methyl side-chains per molecule and further, the nonlinear fraction of said enriched stream preferably comprises less than about 30%, more preferably less than about 10%, more preferably still less than about 1% of molecules having quaternary carbon atoms and less than 50%, preferably less than about 10%, more preferably less than about 1% of molecules having gem-dimethyl substitution.

Process Embodiments Incorporating Hydroformylation (OXQ Reaction)

As noted in the summary, the present invention also has process embodiments involving converting hydrocarbons, via certain sorptive separation selections, into new and useful modified primary OXO alcohols which can be used to make exceptionally soluble sulfates, poly(alkoxy)sulfates, and poly(alkoxylates). These are only illustrative. The modified versions of any other surfactant types known in the art to be derivable from OXO alcohols are, of course, included in the present invention. With respect to such a process embodiment, broadly defined in the summary, a preferred process herein has in stage (A) means comprising one, two or more of said devices and at least two of said beds, at least one of said beds comprising said porous media differentiated relative to the porous media contents of another of said beds by an increased capacity to retain methyl-branched acyclic aliphatic hydrocarbons. Moreover, preferably, said stage (D) comprises a one-step OXO stage wherein said OXO catalyst is a phosphine-coordinated transition metal other than iron.

In more detail, in such a preferred process, at least one of said beds comprises porous media conventional for the manufacture of linear alkylbenzenes, said at least one bed having a connection into said process suitable for at least partially increasing the proportion of methyl-branched acyclic aliphatic hydrocarbons in streams passing to said stage (B) of said process, and suitable for at least partially decreasing the proportion of linear acyclic aliphatic hydrocarbons passing to said stage (B) of said process, said linear acyclic aliphatic hydrocarbons being at least partially being removed as the linear-enriched stream in said stage (A).

Conveniently, in one such process embodiment, said simulated moving bed adsorptive separation means in said stage (A) comprise—one of said device, provided that said device is capable of simulating movement of said porous media in at least two of said at least one bed; or—at least two of said device.

Also encompassed herein is the process wherein there are two of said at least one bed, each comprising a different member of said porous media, each of said at least one bed being controlled by one of said device, and each of said device having a minimum of eight ports for achieving simulated movement of said porous media in said at least one bed. See, for example, FIG. **9** wherein unit SOR 4/5 comprises one type of porous media as defined in more detail elsewhere herein, and unit SOR 5/7 comprises another type. The "devices" referred to can especially be chosen from special rotary valve devices, as described in detail in various patents identified in the "Background Art" section. See also FIG. **8** which, though it illustrates more particularly a process having an alkylation step, more detail of a suitable arrangement of sorptive separation units, rotary valves and ancilliary equipment is shown. It should therefore be understood that the devices, sorption media and equipment are all individually known; it is rather the selection of devices and how they should be connected which is essential for the present inventive purposes to arrive at superior OXO alcohols and the derivative surfactants.

The present invention accordingly also encompasses a process of the OXO-alcohol producing type wherein said linear-enriched stream is present in said stage (A) and said stage (A) comprises. (A-i) adsorptive separation of said hydrocarbon feed into said linear-enriched stream and an intermediate branched-enriched stream and rejection of said linear-enriched stream by means of one of said simulated moving bed adsorptive separation means; followed by (A-ii) adsorptive separation of said intermediate branched-enriched stream into said branched-enriched stream comprising an increased proportion of branched acyclic aliphatic hydrocarbons relative to said intermediate branched-enriched stream, and said reject stream comprising at least an increased proportion of cyclic and/or aromatic hydrocarbons relative to said branched-enriched stream, by means of another of said simulated moving bed adsorptive separation means.

Preferably in such embodiment, all of said beds comprises porous media not conventional for the manufacture of linear alkylbenzenes (for example a SAPO-11 containing unit SOR 5/7 or other equivalent molecular sieve of a pore size larger than is used in making linear alkylbenzenes) said porous media having pore sizes suitable for, and being connected into said process, in a manner consistent with at least partially increasing the proportion of methyl-branched plus linear acyclic aliphatic hydrocarbons in streams passing to said step (B) of said process, and at least partially decreasing the proportion of cyclic, aromatic and, or ethyl-branched or higher, aliphatic hydrocarbons passing to said step (B) of said process, said hydrocarbons other than said linear- and methyl-branched hydrocarbons being at least partially being removed as a reject stream in said stage (A).

Suitably in the OXO-alcohol making embodiments of the present process, said hydrocarbon feed comprises at least about 10% methyl-branched paraffins having molecular weight of at least about 128 and no more than about 282 See the tables elsewhere herein for additional description of suitable feeds.

Crude feed materials in the OXO-alcohol processes herein are desirably distilled before use. For example as non-limitingly illustrated by the distillation unit at the beginning of the processes shown in FIGS. **9**–**18**. In this example the hydrocarbon feed (as it proceeds from such a distillation unit into the remainder of the process) comprises a narrow cut of not more than about three carbon atoms (preferably not more than about two carbon atoms) in the range C10 to C17. Such cuts can be single carbon cuts, two-carbon cuts, three-carbon cuts, or cuts comprising a nonexact range of carbon numbers, such as a one-and one-half carbon cut. Suitable cuts are further illustrated by a C11–C13 cut, a C14–C15 cut, and a Cl5–C17 cut, though it is not intended to exclude other cuts such as a C16.5 cut. Such cuts designated by nonintegral carbon numbers can be generated by any means, such as blending shorter and longer single carbon number fractions. Thus a C16.5 cut can be made by blending C16 and C17 or by blending C14 and C17, etc. Preferred cuts have narrower "spread" of carbon numbers in a blend. Alternatively, the distillation could be performed directly on the olefinic branced enriched stream just before the oxo reaction on the olefinic branced enriched stream to produce the desired cut.

It should of course be understood and appreciated for practical purposes that when distilling hydrocarbons herein, the desirable methyl-branched hydrocarbons will be generally lower in boiling-point than the linear hydrocarbons having equal carbon number. Therefore, a preferred cut boiling in a range intermediate between a linear C15 and a linear C16 paraffin (and thus apparently a cut having non-integral carbon number) will be relatively rich in methyl-branched isomers having a total of 16 carbon atoms which are desirable for the present process.

Very unusually, if not uniquely, for an OXO-alcohol making process, said hydrocarbon feedstock is an adsorptive separation raffinate deriving from a linear alkylbenzene manufacturing process or from a conventional linear detergent alcohol process. In other words, the present invention opens up all manner of new possibilities for combining linear alkylbenzene manufacturing and/or conventional linear detergent alcohol process and OXO alcohol manufacturing in a manner not hitherto accomplished. This results in better utilization of the feeds. Moreover, when using the invention as taught herein, new alkylbenzenes and OXO alcohols are accessible. These can be made on their own, or can be made in any permutation with conventional linear alkylbenzenes and/or OXO alcohols by configuring the plant appropriately using the steps taught herein.

Once the modified primary OXO alcohol has been made, it can of course be converted in the same plant or at a remote facility to another useful derivative. For example, the present process can have the additional stage or stages in sequence selected from: (E) sulfating and neutralizing the product of said stage (D);(F) alkoxylating the product of said stage (D), and (G) alkoxylating, sulfating and neutralizing the product of said stage (D).

Moreover once surfactant derivatives of the above kinds have been made, they can readily be incorporated into all manner of cleaning compositions. For this purpose, colocated in the same facility or remotely situated, the present process can have the additional step of (H) mixing the product of the preceding stages with one or more cleaning product adjunct materials; thereby forming a cleaning product.

Although as will be seen from the Background Art section, various OXO alcohols are already well known, see for example the Shell and/or Sasol processes, it has not previously been suggested to apply the kinds of specific sorptive separation prior to the OXO stage which are specifically identified here. Moreover it has not been suggested to use, at least with respect to detergents, hitherto unuseful parts of streams available from linear alkylbenzene manufacture. From either the crude feed selection, or the use of the specific sorptive separation stages, or both, the composition of the resulting OXO alcohols is changed relative to the Shell and Sasol processes and makes them very useful for the manufacture of surfactants, especially for low wash temperature, demanding solubility (compact granules, tablets) or high water hardness applications. All of this is accomplished with great economy. In view of the compositional changes imparted to the OXO alcohols, the invention also encompasses modified primary OXO alcohol produced by any of the present processes.

Likewise the invention encompasses any consumer cleaning product produced by the above-described processes that include the specific OXO alcohol manufacture shown herein, followed by a stage comprising admixing at least one cleaning product adjunct ingredient.

In other variations, the processes herein include those in which prior to said OXO stage, (D), the product of said stage (B) or (C) is blended with a conventional detergent olefin; or wherein the product of any of said stages (E), (F) or (G) are blended with a conventional detersive surfactant.

Although there are many configurations in which the p resent process makes it possible to prepare concurrently or in alternate processing cycles both modified alkylbenzenes and modified primary OXO alcohols, one such nonlimiting process according to the invention further comprising at least one stage of reacting the product of stage (A) with an aromatic hydrocarbon selected from the group consisting of benzene, toluene and mixtures thereof in the presence of an alkylation catalyst; for making modified (crystallinity-disrupted) alkylbenzenes, said alkylation catalyst has an internal isomer selectivity of from 0 to 40. Ramifications include providing means are provided to route the product of stage (C) to stage (D), to said alkylation step, or to both of said stages in parallel. See the Figures for further illustration.

More generally, the invention also encompasses a detergent or cleaning composition comprising (a) an effective amount of a detersive surfactant selected from alkyl sulfates, alkylpoly(alkoxy)sulfates, alkylpoly(alkoxylates) and mixtures thereof, said surfactant incorporating (preferably in an amount of up to one mole of, more preferably, about one mole of) the R—O— radical of an R=C9–C20 detergent alcohol of formula ROH, wherein R is mixtures of methyl branched and some linear chains and said alcohol is further characterized in that it comprises the product of at least one Fischer-Tropsch process stage or an oligomerization or dimerization or skeletal isomerization stage or olefin and/or paraffin provision stage (e.g., via the above adsorptive separations or alternate processes such as wax hydroisomerization/cracking, Flexicoking®, Fluidcoking®, etc.) and at least one OXO process stage, provided that in at least one stage prior to said OXO process stage there is present a sorptive separation stage having the effect of increasing the proportion of methyl-branched olefin used as feed in said OXO process stage; and (b) one or more adjuncts at least partially contributing to the useful properties of the composition.

Also encompassed herein is a detergent or cleaning, composition comprising (a) an effective amount of a detersive surfactant selected from alkyl sulfates, alkylpoly(alkoxy)sulfates, alkylpoly(alkoxylates) and mixtures thereof, said surfactant incorporating (preferably in an amount of up to one mole of, more preferably about one mole of) the R—O— radical of an R=C9–C20 detergent alcohol of formula ROH, wherein R is mixtures of methyl branched and some linear chains and said alcohol is further characterized in that it comprises the product of any of the hereinabove-described modified primary OXO alcohol making processes; and (b) one or more adjuncts at least partially contributing to the useful properties of the composition.

Cleaning Product Embodiments

Cleaning product embodiments of the present invention include laundry detergents, dishwashing detergents, hard surface cleaners and the like. In such embodiments, the content of modified alkylbenzenesulfonate or surfactant derived from modified primary OXO alcohol produced by the instant process is from about 0.1% to about 99.9%, typically from about 1% to about 50%, and the composition further comprises from about 0.1% to about 99.9%, typically from about 1% to about 50%, of cleaning product adjunct materials such as cosurfactants, builders, enzymes, bleaches, bleach promoters, activators or catalysts, and the like.

The present invention also encompasses a cleaning product formed by the instant process comprising

(a) from about 0.1% to about 99.8%, more typically up to about 50%, of modified alkylbenzenesulfonate surfactant or modified primary OXO alcohol derived surfactant such as modified alkyl sulfate, modified poly(alkoxy)sulfate etc., as prepared herein and

(b) from about 0.00001%, more typically at least about 1%, to about 99.9% of one or more of said cleaning product adjunct materials.

Adjunct materials can vary widely and accordingly can be used at widely ranging levels. For example, detersive enzymes such as proteases, amylases, cellulases, lipases and the like as well as bleach catalysts including the macrocyclic types having manganese or similar transition metals all useful in laundry and cleaning products can be used herein at very low, or less commonly, higher levels.

Other cleaning product adjunct materials suitable herein include bleaches, especially the oxygen bleach types including activated and catalyzed forms with such bleach activators as nonanoyloxybenzenesulfonate and/or tetraacetylethylenediamine and/or any of its derivatives or derivatives of phthaloyiimidoperoxycaproic acid or other imido- or amido-substituted bleach activators including the lactam types, or more generally any mixture of hydrophilic and/or hydrophobic bleach activators (especially acyl derivatives including those of the C6–C16 substituted oxybenzenesulfonates); preformed peracids related to or based on any of the hereinbefore mentioned bleach activators, builders including the insoluble types such as zeolites including zeolites A, P and the so-called maximum aluminum P as well as the soluble types such as the phosphates and polyphosphates, any of the hydrous, water-soluble or water-insoluble silicates, 2,2'-oxydisuccinates, tartrate succinates, glycolates, NTA and many other ethercarboxylates or citrates, chelants including EDTA, S,S'-EDDS, DTPA and phosphonates, water-soluble polymers, copolymers and terpolymers, soil release polymers, cosurfactants including any of the known anionic, cationic, nonionic or zwitterionic types, optical brighteners, processing aids such as crisping agents and/fillers, solvents, antiredeposition agents, silicone/silica and other suds suppressors, hydrotropes, perfumes or pro-perfumes, dyes, photobleaches, thickeners, simple salts and alkalis such as those based on sodium or potassium including the hydroxides, carbonates, bicarbonates and sulfates and the like. When combined with the modified alkylbenzenesulfonate surfactants of the instant process, any of the anhydrous, hydrous, water-based or solvent-borne cleaning products are readily accessible as granules, tablets, powders, flakes, gels, extridates, pouched or encapsulated forms or the like. Accordingly the present invention also includes the various cleaning products made possible or formed by any of the processes described. These may be used in discrete dosage forms, used by hand or by machine, or may be continuously dosed into all suitable cleaning appliances or delivery devices.

Cleaning Products in Detail

References cited herein are incorporated by reference. The surfactant compositions prepared by the processes of the present invention can be used in a wide range of consumer cleaning product compositions including powders, granules, gels, pastes, tablets, pouches, bars, types delivered in dual-compartment containers, spray or foam detergents and other homogeneous or multiphasic consumer cleaning product forms. They can be used or applied by hand and/or can be applied in unitary or freely alterable dosage, or by automatic dispensing means, or are useful in appliances such as washing-machines or dishwashers or can be used in institutional cleaning contexts, including for example, for personal cleansing in public facilities, for bottle washing, for surgical instrument cleaning or for cleaning electronic components. They can have a wide range of pH, for example from about 2 to about 12 or higher, and they can have a wide range of alkalinity reserve which can include very high alkalinity reserves as in uses such as drain unblocking in which tens of grams of NaOH equivalent can be present per 100 grams of formulation, ranging through the 1–10 grams of NaOH equivalent and the mild or low-alkalinity ranges of liquid hand cleaners, down to the acid side such as in acidic hard-surface cleaners. Both high-foaming and low-foaming detergent types are encompassed.

Consumer product cleaning compositions are described in the "Surfactant Science Series", Marcel Dekker, New York, Volumes 1–67 and higher. Liquid compositions in particular are described in detail in the Volume 67, "Liquid Detergents", Ed. Kuo-Yann Lai, 1997, ISBN 0-8247-9391-9 incorporated herein by reference. More classical formulations, especially granular types, are described in "Detergent Manufacture including Zeolite Builders and Other New Materials". Ed. M Sittig, Noves Data Corporation, 1979 incorporated by reference See also Kirk Othmer's Encyclopedia of Chemical Technology

Consumer product cleaning(compositions herein nonlimitingly include:

Light Duty Liquid Detergents (LDL) these compositions include LDL compositions having surfactancy improving magnesium ions (see for example WO 97/00930 A; GB 2,292,562 A; U.S. Pat. No. 5,376,310; U.S. Pat. No. 5,269,974; U.S. Pat. No. 5,230,823; U.S. Pat. No. 4,923,635; U.S. Pat. No. 4,681,704; U.S. Pat. No. 4,316,824; U.S. Pat. No. 4,133,779) and/or organic diamines and/or various foam stabilizers and/or foam boosters such as amine oxides (see for example U.S. Pat. No. 4,133,779) and/or skin feel modifiers of surfactant, emollient and/or enzymatic types including proteases; and/or antimicrobial agents more comprehensive patent listings are given in Surfactant Science Series, Vol 67, pages 240–248.

Heavy Duty Liquid Detergents (HDL): these compositions include both the so-called "structured" or multi-phase (see for example U.S. Pat. No. 4,452,717; U.S. Pat. No. 4,526,709; U.S. Pat. No. 4,530,780, U.S. Pat. No. 4,618,446; U.S. Pat. No. 4,793,943; U.S. Pat. No. 4,659,497; U.S. Pat. No. 4,871,467; U.S. Pat. No. 4,891,147; U.S. Pat. No. 5,006,273; U.S. Pat. No. 5,021,195; U.S. Pat. No. 5,147,576; U.S. Pat. No. 5,160,655) and "non-structured" or isotropic liquid types and can in general be aqueous or nonaqueous (see, for example EP 738,778 A; WO 97/00937 A; WO 97/00936 A, EP 752,466 A; DE 19623623 A; WO 96/10073 A; WO 96/10072 A; U.S. Pat. No. 4.647,393, U.S. Pat. No. 4,648,983; U.S. Pat. No. 4,655,954; U.S. Pat. No. 4,661,280; EP 225,654; U.S. Pat. No. 4,690,771, U.S. Pat. No. 4,744,916; U.S. Pat. No. 4,753,750; U.S. Pat. No. 4,950,424; U.S. Pat. No. 5,004,556; U.S. Pat. No. 5,102,574; WO 94/23009; and can be with bleach (see for example U.S. Pat. No. 4,470,919; U.S. Pat. No. 5,250,212; EP 564,250; U.S. Pat. No. 5,264,143; U.S. Pat. No. 5,275,753; U.S. Pat. No. 5,288,746; WO 94/11483; EP 598,170; EP 598,973; EP 619,368; U.S. Pat. No. 5,431,848; U.S. Pat. No. 5,445,756) and/or enzymes (see for example U.S. Pat. No. 3,944,470; U.S. Pat. No. 4,111,855; U.S. Pat. No. 4,261,868; U.S. Pat. No. 4,287,082; U.S. Pat. No. 4,305,837; U.S. Pat. No. 4,404,115; U.S. Pat. No. 4,462,922; U.S. Pat. No. 4,529,5225; U.S. Pat. No. 4,537,706; U.S. Pat. No. 4,537,707; U.S. Pat. No. 4,670,179; U.S. Pat. No. 4,842,758; U.S. Pat. No. 4,900,475, U.S. Pat. No. 4,908,150; U.S. Pat. No. 5,082,585; U.S. Pat. No. 5,156,773; WO 92/19709; EP 583,534; EP 583,535; EP 583,536; WO 94/04542; U.S. Pat. No. 5,269,960; EP 633,311; U.S. Pat. No. 5,422,030; U.S. Pat. No. 5,431,842; U.S. Pat. No. 5,442,100) or without bleach and/or enzymes Other patents relating to heavy-duty liquid detergents are tabulated or listed in Surfactant Science Series, Vol. 67, pages 309–324.

Heavy Duty Granular Detergents (HDG): these compositions include both the so-called "compact" or agglomerated or otherwise non-spray-dried, as well as the so-called "fluffy" or spray-dried types. Included are both phosphated and nonphosphated types. Such detergents can include the more common anionic-surfactant based types or can be the so-called "high-nonionic surfactant" types in which commonly the nonionic surfactant is held in or on an absorbent such as zeolites or other porous inorganic salts. Manufacture of HDG's is, for example, disclosed in EP 753,571 A; WO 96/38531 A; U.S. Pat. No. 5,576,285; U.S. Pat. No. 5,573,697; WO 96/34082 A; U.S. Pat. No. 5,569,645; EP 739,977 A; U.S. Pat. No. 5,565,422; EP 737,739 A; WO 96/27655 A, U.S. Pat. No. 5,554,587; WO 96/25482 A, WO 96/23048 A; WO 96/22352 A; EP 709,449 A; WO 96/09370 A; U.S. Pat. No. 5,496,487; U.S. Pat. No. 5,489,392 and EP 694,608 A.

"Softergents" (STW): these compositions include the various granular or liquid (see for example EP 753,569 A; U.S. Pat. Nos. 4,140,641; 4,639,321, 4,751,008; EP 315,126; U.S. Pat. Nos. 4,844,821; 4,844,824; 4,873,001; 4,911,852; 5,017,296; EP 422,787) softening-through-the wash types of product and in general can have organic (e.g., quaternary) or inorganic (e.g., clay) softeners.

Hard Surface Cleaners (HSC): these compositions include all-purpose cleaners such as cream cleansers and liquid all-purpose cleaners; spray all-purpose cleaners including glass and tile cleaners and bleach spray cleaners, and bathroom cleaners including mildew-removing, bleach-containing, antimicrobial, acidic, neutral and basic types. See, for example EP 743,280 A; EP 743,279 A. Acidic cleaners include those of WO 96/34938 A.

Bar Soaps and/or Laundry Bars (BS&HW): these compositions Include personal cleansing bars as well as so-called laundry bars (see, for example WO 96/35772 A), including both the syndet and soap-based types and types with softener (see U.S. Pat. No. 5,500,137 or WO 96/01889 A); such compositions can include those made by common soap-making techniques such as plodding and/or more unconventional techniques such as casting, absorption of surfactant into a porous support, or the like. Other bar soaps (see for example BR 9502668, WO 96/04361 A; WO 96/04360 A; U.S. Pat. No. 5,540,852) are also included. Other handwash detergents include those such as are described in GB 2,292,155 A and WO 96/01306 A.

Shampoos and Conditioners (S&C) (see, for example WO 96/37594 A; WO 96/17917 A; WO 96/17590 A; WO 96/17591 A). Such compositions in general include both simple shampoos and the so-called "two-in-one" or "with conditioner" types.

Liquid Soaps (LS): these compositions include both the so-called "antibacterial" and conventional types, as well as those with or without skin conditioners and include types suitable for use in pump dispensers, and by other means such as wall-held devices used institutionally.

Special Purpose Cleaners (SPC): including home dry cleaning systems (see for example WO 96/30583 A; WO 96/30472 A; WO 96/30471 A, U.S. Pat. No. 5,547,476; WO 96/37652 A); bleach pretreatment products for laundry (see EP 751,210 A); fabric care pretreatment products (see for example EP 752,469 A); liquid fine fabric detergent types, especially the high-foaming variety; rinse-aids for dishwashing; liquid bleaches including both chlorine type and oxygen bleach type, and disinfecting agents, mouthwashes, denture cleaners (see, for example WO 96/19563 A; WO 96/19562 A), car or carpet cleaners or shampoos (see, for example EP 751,213 A; WO 96/15308 A), hair rinses, shower gels, foam baths and personal care cleaners (see, for example WO 96/37595 A, WO 96/37592 A; WO 96/37591 A; WO 96/37589 A: WO 96/37588 A; GB 2,297,975 A; GB 2,297,762 A; GB 2,297,761 A; WO 96/17916 A; WO 96/12468 A) and metal cleaners, as well as cleaning auxiliaries such as bleach additives and "stain-stick" or other pre-treat types including special foam type cleaners (see, for example EP 753,560 A; EP 753,559 A; EP 753,558 A; EP 753.557 A, EP 753,556 A) and anti-sunfade treatments (see WO 96/03486 A; WO 96/03481 A; WO 96/03369 A) are also encompassed.

Detergents with enduring perfume (see for example U.S. Pat. No. 5,500,154; WO 96/02490) are increasingly popular.

Process Integration

The present process can be integrated with current LAB manufacturing processes or with conventional linear detergent alcohol process in any convenient manner. For example, conventional erected plant can be switched to produce the modified alkylbenzenes and/or modified primary OXO alcohols in their entirety. Alternately, depending on volumes desired or feedstocks available, for example as effluents from the LAB process or conventional linear detergent alcohol process or based on proximity of feedstock sources from the petrochemical industry, plant for the manufacture of the instant modified alkylbenzenes and/or modified primary OXO alcohols may be erected as an add-on or complement to an existing LAB facility, or as a stand-alone. Both batch and continuous operation of the present process are envisaged.

In one add-on mode, the present invention encompasses steps of making vinylidene olefin and from the vinylidene olefin, modified alkylbenzene or alkyltoluene and/or modified primary OXO alcohol using the steps described in detail hereinabove. The modified alkylbenzene or alkyltoluene is blended at a ratio of from about 1:100 to 100:1, more typically from about 1:10 to about 10:1, for example about 1:5, into a conventional linear alkylbenzene, for example a C11.8 average alkylbenzene or any alkylbenzene produced by the DETAL® process The blend is then sulfonated, neutralized and incorporated into consumer cleaning product compositions. Parallel process stages or alternate process stages lead to modified primary OXO alcohol.

The present invention should not be considered limited by the specifics of its illustration in the specification including the examples given for illustration hereinafter. Most generally, the present invention should be taken to encompass any consumer cleaning composition comprising any surfactant product of any type wherein the hydrophobe of the surfactant has been modified by an approach using the essential teachings of the instant process. The present teachings, especially with respect to the delinearization approach, are believed to be reapplicable, for example, to the manufacture of modified alkyl sulfates and other surfactants.

EXAMPLE 1

Modified Alkylbenzenesulfonate Prepared Via Branched Hydrocarbon-containing Feeds Sourced from Jet/Diesel; with Separation Over SAPO-11, Dehydrogenation; Alkylation Over H-mordenite; Sulfonation Using Sulfur Trioxide/Air; and Neutralization

A suitable feed is obtained in the form of a jet/diesel distillation cut from kerosene. This feed contains paraffinic branched and linear hydrocarbons, wherein the linear hydrocarbons are of suitable chainlength for LAB manufacture and wherein the branched hydrocarbons include at least about 10% of methyl branched paraffins along with cyclic hydrocarbons, aromatics and other impurities. This stream is passed continuously to two adsorptive separation units, connected as shown in FIG. **8** and FIG. **1** wherein unit AC1 of detail FIG. **8** is loaded with 5 Angstrom Ca zeolite as used in conventional linear alkylbenzene manufacture and unit AC2 of detail FIG. **8** is loaded with the silicoaluminophiosphate SAPO-11. The units AC1 and AC2 along with the associated rotary valve devices, raffinate columns and extract columns (RC and EC) and condensers (shown as unlabeled horizontal tanks in FIG. **8**.) and other means shown, though connected in unique manner, are of construction generally in accordance with units licensable and commercially available through UOP Corp. (MOLEX® units). The adsorbate (extract) from the Ca zeolite adsorptive unit AC1 is rejected and the raffinate is passed continuously to the second adsorptive separation unit AC2 containing the SAPO-11. The branched-enriched stream taken from unit AC2 as adsorbate or extract is passed to a standard commercial LAB process dehydrogenation unit provided by UOP Corp. (PACOL® process) charged with a standard LAB dehydrogenation catalyst (DeH 5® or DeH 7® or similar) proprietary to UOP Corp. After dehydrogenation under conventional LAB-making process conditions, the hydrocarbons are passed continuously to an alkylation unit which is otherwise conventional but is charged with H-mordenite (ZEOCAT® FM 8/25 H) where alkylation proceeds continuously at a temperature of about 200° C. with discharge on reaching a completion of at least about 90%, that is, a conversion of the input hydrocarbon (olefins) of at least about 90%. This produces a modified alkylbenzene. In optional variations, the above procedure can be repeated except with discharge on reaching a conversion (based on olefin) to the desired modified alkylbenzene of at least about 80%. A recycle of paraffins is obtained by distillation at the back-end of the alkylation unit and the recycle is passed back to the dehydrogenator. The process to this point includes the steps and streams of FIG. **1**. The modified alkylbenzene can be further purified by additional conventional distillation (such distillative steps are not shown in FIG. **1**). The distilled modified alkylbenzene mixture is sulfonated batchwise or continuously, at a remote facility if desired, using sulfur trioxide as sulfonating agent. Details of sulfonation using a suitable air/sulfur trioxide mixture are provided in U.S. Pat. No. 3,427,342, Chemithon. The modified alkylbenzenesulfonlic acid product of the preceding step is neutralized with sodium hydroxide to give modified alkylbenzene sulfonate, sodium salt mixture.

EXAMPLE 2

Modified Alkylbenzenesulfonate Prepared Via Hydrocarbon Feed Sourced from MOLEX® Effluent, Separation Over SAPO-11, Dehydrogenation Using Standard UOP Method, Alkylation Over H-mordenite, Sulfonation Using Sulfur Trioxide/Air, and Neutralization

A suitable feedstock is obtained in the form of effluent or raffinate from an LAB plant, specifically the MOLEX® process unit of such a plant. This raffinate contains a high proportion of branched paraffinic hydrocarbons along with undesirable cyclic hydrocarbons, aromatics and other impurities. This raffinate is passed continuously to an adsorptive separation unit constructed conventionally, e.g., after the manner of a MOLEX® unit, but having a charge of SAPO-11. This unit operates under conditions generally similar to the MOLEX® unit as used in linear alkylbenzene manufacture and resembles the unit AC2 described in Example 1. The raffinate or effluent from the SAPO-11 adsorptive unit is rejected and the adsorbate or extract now meeting the invention definition of a branched-enriched stream is passed continuously to a standard commercial LAB process dehydrogenation unit provided by UOP Corp. (PACOL® process) charged with a standard LAB dehydrogenation catalyst (e.g., DeH 7®) proprietary to UOP Corp. After dehydrogenation under conventional LAB-making process conditions, the hydrocarbons are passed continuously to an alkylation unit which is otherwise conventional but is charged with H-mordenite (ZEOCAT® FM 8/25 H) where alkylation proceeds continuously at a temperature of about 200° C. with discharge on reaching an alkylating agent conversion of at least about 90%. The modified alkylbenzene mixture is purified by conventional distillation and branched paraffins are recycled to the dehydrogenation unit. Steps in the process to this point follow FIG. **4**.

The distilled modified alkylbenzene mixture produced in process to this point is sulfonated batchwise or continuously, at a remote facility if desired, using sulfur trioxide as sulfonating agent. Details of sulfonation using a suitable air/sulfur trioxide mixture are provided in U.S. Pat. No. 3,427,342, Chemithon The modified alkylbenzenesulfonic acid product of the preceding step is neutralized with sodium hydroxide to give modified alkylbenzene sulfonate, sodium salt mixture.

EXAMPLE 3

Modified Alkylbenzenesulfonate Prepared Via Hydrocarbon Feed Sourced from MOLEX® Effluent, Separation Over Pyrolyzed Poly (vinylidene chloride), Dehydrogenation Using Standard UOP Method, Alkylation Over H-ZSM-12, Sulfonation Using Sulfur Trioxide/Air and Neutralization

A suitable feedstock is obtained in the form of raffinate from an LAB plant, specifically the MOLEX® process unit of such a plant. This raffinate contains branched paraffinic hydrocarbons along with cyclic hydrocarbons, aromatics and other undesired impurities. This raffinate is passed continuously to an adsorptive separation unit of conventional construction, e.g., MOLEX® type, not conventionally being incorporated in LAB plant design and hereinafter termed the "SARAN® unit" having a charge of pyrolyzed poly(vinylidene chloride), sieve diameter >5 Angstrom, manufactured according to Netherlands Application NL 7111508 published Oct. 25, 1971. The "SARAN unit" operates under conditions similar to the MOLEX® unit. The Raffinate from the "SARAN unit" is rejected and the adsorbate is passed continuously to a standard commercial LAB process dehydrogenation unit provided by UOP Corp. (PACOL® process) charged with a standard LAB dehydrogenation catalyst such as DeH 7® proprietary to UOP Corp. After dehydrogenation under conventional LAB-making process conditions, the hydrocarbons are passed continuously to an alkylation unit which is otherwise conventional but is charged with H-ZSM 12 where alkylation proceeds continuously at a temperature of about 200° C. with discharge on reaching a conversion of the input hydrocarbon of at least about 90%. The modified alkylbenzene mixture produced in the preceding step is distilled and sulfonated batchwise or continuously using sulfur trioxide as sulfonating agent. Details of sulfonation using a suitable air/sulfur trioxide mixture are provided in U.S. Pat. No. 3,427,342, Chemithon. The modified alkylbenzenesulfonic acid product of the preceding step is neutralized with sodium hydroxide to give modified alkylbenzene sulfonate, sodium salt mixture.

EXAMPLE 4

Modified Alkylbenzenesulfonate Prepared Via Hydrocarbon Feed from Urea Clathration, Separation Over SAPO-11, Dehydrogenation Using Pt Catalyst, Alkylation Over Acidic Zeolite Beta, Sulfonation Using Sulfur Trioxide/Air and Neutralization

A suitable feedstock is obtained from kerosene by urea clathration which is used to remove a fraction rich in the more commercially valuable linear hydrocarbons. See U.S. Pat. No. 3,506,569. The low-grade branched effluent from the urea clathration stage is a suitable hydrocarbon feed for the present process. It is stripped of any activator solvent such as methanol, if present, and is passed continuously to an adsorptive separation unit constructed in any conventional manner, for example after the fashion of MOLEX° process units, but differently charged, having a charge of SAPO-11. The SAPO-11 unit operates under conditions similar to a standard MOLEX® process unit. The raffinate from the SAPO-11 unit is rejected and the adsorbate is passed continuously to a standard commercial LAB process dehydrogenation unit provided by UOP Corp. (PACOL® process) charged with a nonproprietary Platinum dehydrogenation catalyst. After dehydrogenation under conventional LAB-making process conditions, the hydrocarbons are passed continuously to an alkylation unit which is otherwise conventional but is charged with Zeocat PB/HE where alkylation proceeds continuously at a temperature of about 200° C. with discharge on reaching a conversion of the input hydrocarbon of at least about 90%. The modified alkylbenzene mixture produced in the preceding step is sulfonated batchwise or continuously using sulfur trioxide as sulfonating agent. Details of sulfonation using a suitable air/sulfur trioxide mixture are provided in U.S. Pat. No. 3,427,342, Chemithon. The modified alkylbenzenestilfonic acid product of the preceding step is neutralized with sodium hydroxide to give modified alkylbenzene sulfonate, sodium salt mixture.

EXAMPLE 5

Modified Alkylbenzenesulfonate Prepared Via Hydrocarbon Feed from Kerosene Cut from a High Paraffinic Petroleum Source, Separation Over Grafted Nonacidic Zeolite, Dehydrogenation Using DeH 9® Catalyst, Alkylation Over H-mordenite, Sulfonation Using Chlorosulfonic Acid, and Neutralization

A jet/kerosene cut is taken from a low-viscosity crude, e.g., Brent light. This is passed continuously to an adsorptive separation unit constructed in any conventional manner, for lo example after the fashion of MOLEX® process units, but differently charged, having a charge of grafted zeolite prepared in accordance with U.S. Pat. No. 5,326,928, The unit operates under conditions similar to a conventionally charged MOLEX® unit The raffinate from this unit is rejected and the adsorbate is passed continuously to a standard commercial LAB process dehydrogenation unit provided by UOP Corp (PACOL® process) charged with a standard LAB dehydrogenation catalyst DeH 9® proprietary to UOP Corp. After dehydrogenation under conventional LAB-making process conditions, the hydrocarbons are passed continuously to an alkylation unit which is otherwise conventional but is charged with H-mordenite (ZEOCAT FM 8/25 H) where alkylation proceeds continuously at a temperature of about 200° C. with discharge on reaching a conversion of the input hydrocarbon of at least about 90%. The modified alkylbenzene mixture produced in the preceding step is sulfonated batchwise or continuously using sulfur trioxide as sulfonating agent. Details of sulfonation using a suitable air/sulfur trioxide mixture are provided in U.S. Pat. No. 3,427,342, Chermithon. The modified alkylbenzenesulfonic acid product of the preceding step is neutralized with sodium hydroxide to give modified alkylbenzene sulfonate, sodium salt mixture.

EXAMPLE 6

Cleaning Product Composition

10% by weight of modified alkylbenzenesulfonate sodium salt product of any of the foregoing exemplified processes is combined with 90% by weight of an agglomerated compact laundry detergent granule.

EXAMPLE 7

Cleaning Product Composition

In this Example, the following abbreviation is used for a modified alkylbenzene sulfonate, sodium salt form or potassium salt form, prepared according to any of the preceding process examples: MAS

The following abbreviations are used for cleaning product adjunct materials:

Cxy Amine Oxide	Alkyldimethylamine N-Oxide RN(O)Me2 of given chainlength Cxy where average total carbon range of the non-methyl alkyl moiety R is from 10+x to 10+y
Amylase	Amylolytic enzyme of activity 60KNU/g sold by NOVO Industries A/S under the tradename Termamyl 60T Alternatively, the amylase is selected from Fungamyl ®, Duramyl ®, BAN ®, and α amylase enzymes described in WO95/26397 and in co-pending application by Novo Nordisk PCT/DK96/00056
APA	C8–C10 amido propyl dimethyl amine
Cxy Betaine	Alkyldimethyl Betaine having an average total carbon range of alkyl moiety from 10+x to 10+y
Bicarbonate	Anhydrous sodium bicarbonate with a particle size distribution between 400 μm and 1200 μm
Borax	Na tetraborate decahydrate
BPP	Butoxy - propoxy - propanol
Brightener 1	Disodium 4,4'-bis(2-sulphostyryl)biphenyl
Brightener 2	Disodium 4,4'-bis(4-anilino-6-morpholino-1,3,5-triazin-2-yl)amino) stilbene-2:2'-disulfonate
$CaCl_2$	Calcium chloride
Carbonate	Na_2CO_3 anhydrous, 200 μm–900 μm
Cellulase	Celluloytic enzyme, 1000 CEVU/g, NOVO, Carezyme ®
Citrate	Trisodium citrate dihydrate, 86.4%, 425 μm–850 μm
Citric Acid	Citric Acid, Anhydrous
CMC	Sodium carboxymethyl cellulose
CxyAS	Alkyl sulfate, Na salt or other salt if specified having an average total carbon range of alkyl moiety from 10+x to 10+y
CxyEz	Commercial linear or branched alcohol ethyoxylate (not having mid-chain methyl branching) and having an average total carbon range of alkyl moiety from 10+x to 10+y average z moles of ethylene oxide
CxyEzS	Alkyl ethoxylate sulfate, Na salt (or other salt if specified) having an average total carbon range of alkyl moiety from 10+x to 10+y and an average of z moles of ethylene oxide
Diamine	Alkyl diamine., e.g., 1,3 propanediamine, Dytek EP, Dytek A, (Dupont) or selected from dimethyl aminopropyl amine; 1,6-hexane diamine; 1,3 propane diamine, 2-methyl, 1,5 pentane diamine; 1,3-pentanediamine; 1-methyl-diaminopropane; 1,3 cyclohexane diamine; 1,2 cyclohexane diamine
Dimethicone	40(gum)/60(fluid) wt. Blend of SE-76 dimethicone gum (G.E. Silicones Div)/dimethicone fluid of viscosity 350 cS
DTPA	Diethylene triamine pentaacetic acid
DTPMP	Diethylene Triamine penta (methylene phosphonate), Monsanto (Dequest 2060)
Endolase	Endoglucanase, activity 3000 CEVU/g. NOVO
EtOH	Ethanol
Fatty Acid (C12/18)	C12-C18 fatty acid
Fatty Acid (C12/14)	C12-C14 fatty acid
Fatty Acid (C14/18)	C14-C18 fatty acid
Fatty Acid (RPS)	Rapeseed fatty acid
Fatty Acid (TPK)	Topped palm kernel fatty acid
Formate	Formate (Sodium)
HEDP	1,1-hydroxyethane diphosphonic acid
Hydrotrope	selected from sodium, potassium, Magnesium, Calcium, ammonium or water-soluble substituted ammonium salts of toluene sulfonic acid, naphthalene sulfonic acid, cumene sulfonic acid, xylene sulfonic acid.
Isofol 12	X12 (average) Guerbet alcohols (Condea)
Isofol 16	C16 (average) Guerbet alcohols (Condea)
LAS	Linear Alkylbenzene Sulfonate (e.g., C11.8, Na or K salt)

-continued

Lipase	Lipolytic enzyme, 100kLU/g, NOVO, Lipolase ®. Alternatively, the lipase is selected from: Amano-P; M1 Lipase ®; Lipomax ®; D96L - lipolytic enzyme variant of the native lipase derived from Hemicola lanuginosa as described in U.S. Serial No. 08/341,826; and the Humicola lanuginosa strain DSM 4106.
LMFAA	C12–14 alkyl N-methyl glucamide
MA/AA	Copolymer 1.4 maleic/acrylic acid, Na salt, avg mx. 70,000.
MBAxEy	Mid-chain branched primary alkyl ethoxylate (average total carbons = x, average EO = y)
MBAxEyS	Mid-chain branched or modified primary alkyl ethoxylate sulfate, Na salt (average total carbons = x, average EO = y) according to the invention (see Example 9)
MBAyS	Mid-chain branched primary alkyl sulfate, Na salt (average total carbons = y)
MEA	Monoethanolamine
Cxy MES	Alkyl methyl ester sulfonate, Na salt having an average total carbon range of alkyl moiety from 10+x to 10+y
$MgCl_2$	Magnesium chloride
MnCAT	Macrocyclic Manganase Bleach Catalyst as in EP 544,440 A or, preferably, use $[Mn(Beyclam)Cl_2]$ wherein Beyclam = 5,12-dimethyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane or a comparable bridged tetra-aza macrocycle
NaDCC	Sodium dichloroisocyanurate
NaOH	Sodium hydroxide
Cxy NaPS	Paraffin sulfonate, Na salt having an average total carbon range of alkyl moiety from 10+x to 10+y
NaSKS-6	Crystalline layered silicate of formula δ-$Na_2Si_2O_5$
NaTS	Sodium toluene sulfonate
NOBS	Nonanoyloxybenzene sulfonate, sodium salt
LOBS	C12 oxybenzenesulfonate, sodium salt
PAA	Polyacrylic Acid (mw = 4500)
PAE	Ethoxylated tetracthylene pentamine
PAEC	Methyl quarternized ethoxylated dihexylene triamine
PBI	Anhydrous sodium perborate bleach of nominal formula $NaBO_2.H_2O_2$
PEG	Polyethylene glycol (mw = 4600)
Percarbonate	Sodium Percarbonate of nominal formula $2Na_2CO_3.3H_2O_2$
PG	Propanediol
Photobleach	Sulfonated Zinc Phthalocyanime encapsulated in dextrin soluble polymer
PIE	Ethoxylated polyethyleneimine, water-soluble
Protease	Proteolytic enzyme, 4KNPU/g, NOVO, Savinase ®, Alternatively, the protease is selected from: Maxatase ®; Maxacal ®; Maxapem 15 ®; subtilisin BPN and BPN; Protease B; Protease A; Protease D; Primase ®; Durazym ®; Opticlean ®; and Optimase ®; and Alcalase ®
QAS	$R_2.N^+(CH_3)_N((C_2H_4O)yH)z$ with $R_2 = C_8$–C_{18} $x+z = 3$, $x = 0$ to 3, $z = 0$ to 3, $y = 1$ to 15
Cxy SAS	Secondary alkyl sulfate, Na salt having an average total carbon range of alkyl moiety from 10+x to 10+y
Silicate	Sodium Silicate, amorphous (SiO_2:Na_2O: 2.0 ratio)
Silcone antifoam	Polydimethylsiloxane foam controller + siloxane-oxyalkylene copolymer as dispersing agent: ratio of foam controller:dispersing agent = 10:1 to 100:1 or, combination of fumed silica and high viscosity polydimethylisiloxane (optionally chemically modified)
Solvent	nonaqueous solvent e.g., hexylene glycol. see also propylene glycol
SRP 1	Sulfobenzoyl end capped esters with oxyethylene oxy and terephthaloyl backbone
SRP 2	Sulfonated ethoxylated terephthalate polymer
SRP 3	Methyl capped ethoxylated terephthalate polymer
STPP	Sodium tripolyphosphate, anhydrous
Sulfate	Sodium sulfate, anhydrous
TAED	Tetraacetylethylenediamine
TFA	c16–18 alkyl N-methyl glucamide
Zeolite A	Hydrated Sodium Aluminosilicate, $Na_{12}(AlO_2SiO_2)_{12}$. $27H_2O$; 0.1–10 μm
Zeolite MAP	Zeolite (Maximum aluminum P) detergent grade (Crosfield)

Typical ingredients often referred to as "minors" can include perfumes, dyes, pH trims etc.

The following example is illustrative of the present invention, but is not meant to limit or otherwise define its scope. All parts, percentages and ratios used are expressed as percent weight uniess otherwise noted. The following laundry detergent compositions A to F are prepare in accordance with the invention.

	A	B	C	D	E	F
MAS	22	16.5	11	1–5.5	10–25	5–35
Any Combination of: C45AS C45E1S LAS C26 SAS C47 NaPS C48 MES MBA16.5S MBA15.5E2S	0	1–5.5	11	16.5	0–5	0–10
QAS	0–2	0–2	0–2	0–2	0–4	0
C23E6.5 or C45E7	1.5	1.5	1.5	1.5	0–4	0–4
Zeolite A	27.8	0	27.8	27.8	20–30	0
Zeolite MAP	0	27.8	0	0	0	0
STPP	0	0	0	0	0	5–65
PAA	2.3	2.3	2.3	2.3	0–5	0–5
Carbonate	27.3	27.3	27.3	27.3	20–30	0–30
Silicate	0.6	0.6	0.6	0.6	0–2	0–6
PB1	1.0	1.0	0–10	0–10	0–10	0–20
NOBS	0–1	0–1	0–1	0.1	0.5–3	0–5
LOBS	0	0	0–3	0	0	0
TAED	0	0	0	2	0	0–5
MnCAT	0	0	0	0	2 ppm	0–1
Protease	0–0.5	0–0.5	0–0.5	0–0.5	0–0.5	0–1
Cellulase	0–0.3	0–0.3	0–0.3	0–0.3	0–0.5	0–1
Amylase	0–0.5	0–0.5	0–0.5	0–0.5	0–1	0–1
SRP 1 or SRP 2	0.4	0.4	0.4	0.4	0–1	0–5
Brightener 1 or 2	0.2	0.2	0.2	0.2	0–0.3	0–5
PEG	1.6	1.6	1.6	1.6	0–2	0–3
Silicone Antifoam	0.42	0.42	0.42	0.42	0–0.5	0–1
Sulfate, Water, Minors	to 100%	to 100%	to 100%	to 100%	to 100%	to 100%
Density (g/L)	400–700	600–700	600–700	600–700	600–700	450–750

EXAMPLE 8

Cleaning Product Compositions

The following liquid laundry detergent compositions A to E are prepared in accord with the invention. Abbreviations are as used in the preceding Examples.

	A	B	C	D	E
MAS	1–7	7–12	12–17	17–22	1–35
Any combination of: C25E1.8–2.5S MBA15.5E1.8S MBA15.5S C25AS (linear to high 2-alkyl) C47 NaPS C26 SAS LAS C26 MES	15–21	10–15	5–10	0–5	0–25
LMFAA	0–3.5	0–3.5	0–3.5	0–3.5	0–8
C23E9 or C23E6.5	0–2	0–2	0–2	0–2	0–8
APA	0–0.5	0–0.5	0–0.5	0–0.5	0–2
Citric Acid	5	5	5	5	0–8
Fatty Acid (TPK or C12/14)	2	2	2	2	0–14
EtOH	4	4	4	4	0–8
PG	6	6	6	6	0–10
MEA	1	1	1	1	0–3
NaOH	3	3	3	3	0–7
Hydrotrope or NaTS	2.3	2.3	2.3	2.3	0–4
Formate	0.1	0.1	0.1	0.1	0–1
Borax	2.5	2.5	2.5	2.5	0–5
Protease	0.9	0.9	0.9	0.9	0–1.3
Lipase	0.06	0.06	0.06	0.06	0–0.3
Amylase	0.15	0.15	0.15	0.15	0–0.4
Cellulase	0.05	0.05	0.05	0.05	0–0.2
PAE	0–0.6	0–0.6	0–0.6	0–0.6	0–2.5
PIE	1.2	1.2	1.2	1.2	0–2.5
PAEC	0–0.4	0–0.4	0–0.4	0–0.4	0–2
SRP 2	0.2	0.2	0.2	0.2	0–0.5
Brightener 1 or 2	0.15	0.15	0.15	0.15	0–0.5
Silicone antifoam	0.12	0.12	0.12	0.12	0–0.3
Fumed Silica	0.0015	0.0015	0.0015	0.0015	0–0.003
Perfume	0.3	0.3	0.3	0.3	0–0.6
Dye	0.0013	0.0013	0.0013	0.0013	0–0.003
Moisture/minors	Balance	Balance	Balance	Balance	Balance
Product pH (10% in DI water)	7.7	7.7	7.7	7.7	6–9.5

EXAMPLE 9

In the present Example, a branched-enriched hydrocarbon stream is made and it is dehydrogenated, subjected to hydroformylation to make a modified primary OXO alcohol, ethoxylated and sulfated.

A suitable crude hydrocarbon feed is obtained in the form of a jet/diesel or kerosene distillation cut. This feed is low in sulfur, nitrogen and aromatics (to the extent that these are known to have some adverse effect on lifetime of MOLEX® and OLEX® adsorbent beds) and contains paraffinic branched and linear hydrocarbons, wherein the linear hydrocarbons are of suitable chainlength for detergent manufacture and wherein the branched hydrocarbons include at least about 10% of methyl branched paraffins, along with cyclic hydrocarbons, aromatics and other impurities.

The crude hydrocarbon feed is distilled to obtain a two-carbon cut at about C14–C15. This forms a suitable hydrocarbon feed for the rest of the process See FIG. **10**, stream **1**.

The distilled hydrocarbon feed is passed continuously to two adsorptive separation units, connected as shown in FIG. **10** wherein unit SOR 4/5 is loaded with 5 Angstrom Ca zeolite as used in conventional linear alkylbenzene manufacture, and unit SOR 5/7 is loaded with the silicoaluminophlosplhate SAPO-11. The general construction of the units SOR 4/5 and SOR 5/7 and ancilliary equipment not shown in FIG. **10** is in accordance with units licensable and commercially available through UOP Corp. (MOLEX® units). Not shown are the desorbent systems and ancillary distillation and recovery columns. The linear-enriched stream (stream **6** in FIG. **10**, rich in linear hydrocarbon) from the Ca zeolite MOLEX® unit SOR 4/5 is rejected and the intermediate branched-enriched stream (stream **2** in FIG. **10**, enriched in branched hydrocarbon) is passed continuously to the second adsorptive separation unit SOR 5/7 containing the SAPO-11. The branched-enriched stream taken from unit SOR 5/7 as adsorbate or extract (stream **3** in FIG. **10**, more branched hydrocarbon) is passed to a standard commercial LAB process dehydrogenation unit (DEH in FIG. **10**) provided by UOP Corp. (PACOL® process) charged with a standard dehydrogenation catalyst (DeH 5® or DeH 7® or similar) proprietary to UOP Corp. After partial dehydrogenation (up to about 20%) under conventional LAB olefin feed preparation process conditions, the branched-enriched olefin/paraffin mixtures (stream **4** in FIG. **10**) are passed continuously to DEFINE® and PEP® process units licensed from UOP Corp. These units hydrogenate diolefin impurity to monoolefin and help reduce the content of aromatic impurities, respectively. The resulting purified olefin/paraffin stream (**54** in FIG. **10**) now passes to an OLEX® process unit licensed from UOP, charged with olefin separation sorbent proprietary to UOP Corp. After olefin separation from unreacted paraffins (the latter are recycled as stream **8** in FIG. **10**), the branched-enriched olefinic hydrocarbons (stream **55** in FIG. **10**) are passed continuously to an OXO reaction unit operating with a 2–2.5:1 H2:CO ratio and using a pressure of from about 60–90 atm. and a temperature of about 170° C.—about 210° C. and charged with a cobalt organophosphine complex OXO proceeds continuously with discharge on reaching a selectivity to the modified primary OXO alcohol of at least about 90%, and essentially all the olefin of the input stream has reacted. This produces a modified primary OXO alcohol according to the invention. A small amount of reduction also occurs to form paraffin. The paraffins are separated by distillation and can be recycled to the dehydrogenator. The process to this point includes the steps and streams of FIG. **10**. The modified primary OXO alcohol (stream **57** in FIG. **10**) is ethoxylated to an average of one mole of ethylene oxide content. Alternatively ethoxylation, propoxylation etc. can be done using differing amounts of alkylene oxide to produce the desired alkoxylate. This is done batchwise or continuously, at a remote facility if desired, using ethylene oxide and the usual base catalyst (see Schonfeldt, Surface Active Ethylene Oxide Adducts, Pergamon Press, N.Y., 1969) Now the ethoxylated modified OXO alcohol is treated batchwise or continuously with sulfur trioxide as sulfating agent (See "Sulphonation Technology in the Detergent Industry", W. de Groot, Kluwer Academic Publishers, London, 1991). The product of the preceding step is neutralized with sodium hydroxide to give modified alkyl ethoxysulfate, sodium salt, according to the invention. In variations of the above example, alkyl chain length of the hydrocarbon can be varied so as to produce the desired chainlength modified OXO alcohol derived surfactants as used in the formulation Examples. In a further variation, the modified OXO alcohol can be sulfated without any prior alkoxylation.

EXAMPLE 10

A non-limiting example of bleach-contain nonaqueous liquid laundry detergent is prepared having the composition as set forth in the following Table.

TABLE

Component	Wt. %	Range (% wt.)
Liquid Phase		
LAS	25.0	18–35
C24E5 or MBA14.3E5 (Example 9)	13.6	10–20
Solvent or Hexylene glycol	27.3	20–30
Perfume	0.4	0–1.0
MBA14.4E1S (Example 9)	2.3	1–3.0
Solid Phase		
Protease	0.4	0–1.0
Citrate	4.3	3–6
PB1	3.4	2–7
NOBS	8.0	2–12
Carbonate	13.9	5–20
DTPA	0.9	0–1.5
Brightener 1	0.4	0–0.6
Silicone antifoam	0.1	0–0.3
Minors	Balance	—

The resulting composition is an anhydrous heavy duty liquid laundry detergent which provides excellent stain and soil removal performance when used in normal fabric laundering operations.

EXAMPLE 11

Liquid detergent compositions are made according to the followings.

	A	B	C	D
MBA14.4E1S (Example 9)	2	8	7	5
MBA14.4S (Example 9)	15	12	10	8
C24 Amine Oxide	—	—	—	2
C25AS	6	4	6	8
LMFAA	0–5	0–4	0–3	0–3
C24E5	6	1	1	1
Fatty acid (12/18)	11	4	4	3
Citric acid	1	3	3	2
DTPMP	1	1	1	0.5
MEA	8	5	5	2
NaOH	1	2.5	1	1.5
Solvent or PG	14.5	13.1	10.0	8
EtOH	1.8	4.7	5.4	1
Amylase	0.3	0.3	0.4	0.4
Lipase	0.15	0.15	0.15	0.15
Protease	0.5	0.5	0.5	0.5)
Endolase	0.05	0.05	0.05	0.05
Cellulase	0.09	0.09	0.09	0.09
SRP3	0.5	—	0.3	0.3
Borax	2.4	2.8	2.8	2.4
Hydrotrope	—	3	—	—
Isofol 12	1	1	1	1
Silicone antifoam	0.3	0.3	0.3	0.3
Water & minors	Up to 100%			

The above liquid detergent compositions (A–D) are found to be very efficient in the removal of a wide rang,e of stains and soils from fabrics under various usage conditions.

EXAMPLE 12

The following compositions (E to J) are heavy duty liquid laundry detergent compositions according to the present invention.

	Example #:					
	E	F	G	H	I	J
MBA-14.4E0.8S (Example 9)	17	15	7.0	7.0	12	12
C35E3S/C25E3S	2.0	9.0	—	—	7.0	7.0
C25E2.5S	—	—	12.0	12.0	—	—
LMFAA	6.0	5.0	0	0	4.0	0
C35E7	6.0	1.0	—	—	—	—
C23E9	—	—	2.0	1.0	5.0	5.0
APA	—	1.5	—	2.0	—	2.5
Fatty Acid (C12/C14)	7.5	1.1	2.0	4.0	5.0	5.0
Fatty Acid (C14/C18)	3.0	3.5	—	—	—	—
Citric Acid	1.0	3.5	3.0	3.0	3.0	3.0
Protease	0.6	0.6	0.9	0.9	1.2	1.2
Lipase	0.1	0.1	0.1	0.1	0.2	0.2
Amylase	0.1	0.1	0.1	0.1	—	0.1
Cellulase	0.03	0.03	0.05	0.05	0.2	0.2
Endolase	0.1	0.1	—	—	—	—
Brightener 2	0.1	0.1	—	—	—	—
Borax	3.0	3.0	3.5	3.5	4.0	4.0
MEA	8.0	4.0	1.0	1.5	7.0	7.0
NaOH	1.0	4.0	3.0	2.5	1.0	1.0
PG	12.0	12.0	7.5	7.5	7.0	7.0
EtOH	1.0	1.0	3.5	3.5	6.0	6.0
Hydrotrope	—	—	2.5	2.5	—	—
Minors	Balance	Balance	Balance	Balance	Balance	Balance

EXAMPLE 13

Aqueous based heavy duty liquid laundry detergent compositions K to O which comprise the mid-chain branched surfactants of the present invention are presented below.

Ingredient	K	L	M	N	O
MBA14.4E0.8S (Example 9)	10	12	14	16	20
C25E1.8S	10	8	6	4	0
C23E9	2	2	2	2	2
LMFAA	5	5	5	5	0
Citric acid	3	3	3	3	5
Fatty acid (TPK, RPS or C12/14)	2	2	2	2	0
PAE	1	1	1.2	1.2	0.5
PG	8	8	8	8	4.5
EtOH	4	4	4	4	2
Borax	3.5	3.5	3.5	3.5	2
Hydrotrope	3	3	2	3	0
pH =	8.0	8.0	8.0	8.0	7.0
water and minors	balance 100%	balance 100%	balance 100%	balance 100%	balance 100%

EXAMPLE 14

The following aqueous liquid laundry detergent compositions P to T are prepared in accord with the invention:

	P	Q	R	S	T
MBA14.4E1S and/or MBA14.4S (Example 9)	1–7	7–12	12–17	17–22	1–35
Any combination of: C25E1.8–2.5S C25AS (linear to high 2-alkyl) C47 NaPS C26 SAS LAS C26 MES	15–21	10–15	5–10	0–5	0–25
LMFAA	0–3.5	0–3.5	0–3.5	0–5	0–8
C23E9 or C23E6.5	0–2	0–2	0–2	0–2	0–8
APA	0.5	1	1	1.5	0.5–2
Citric Acid	5	5	5	5	0–8
Fatty Acid (TPK, RPS or C12/14)	2	2	2	10	0–14
EtOH	4	4	4	4	0–8
PG	6	6	6	6	0–10
MEA	1	1	1	1	0–3
NaOH	3	3	3	3	0–7
Hydrotrope	2.5	2	1.5	1	0–4
Borax	2.5	2.5	2.5	2.5	0–5
Protease	0.5	0.7	0.9	0.9	0–1.3
Lipase	0.0	0.06	0.15	0.3	0–0.3
Amylase	0.15	0.2	0.25	0.3	0–0.4
Cellulase	0.05	0.05	0.2	0.3	0–0.2
PAE	0–0.6	0–0.6	0–0.6	0–0.6	0–2.5
PIE	1.2	1.2	1.2	1.2	0–2.5
PAEC	0–0.4	0–0.4	0–0.4	0–0.4	0–2
SRP 2	0.2	0.2	0.2	0.2	0–0.5
Brightener 1 or 2	0.15	0.15	0.15	0.15	0–0.5
Silicone antifoam	0.12	0.12	0.12	0.12	0–0.3
Water and minors	Balance	Balance	Balance	Balance	Balance
Product pH (10% in DI water)	7.7	7.7	7.7	7.7	6–9.5

EXAMPLE 15

Light-duty liquid dishwashing detergent compositions comprising the modified primary OXO alcohol derived surfactants of the present invention are prepared:

Ingredient	Wt. % A	Wt. % B	Wt. % C	Wt. % D
MBA13.5E0.6S (Example 9)	5	10	20	30
MBA12.5E9 (Example 9)	1	1	1	1
C23E1S	25	20	10	0
LMFAA	4	4	4	4
C24 Amine Oxide	4	4	4	4
EO/PO Block Co-polymer - Tetronic ® 704	0.5	0.5	0.5	0.5
EtOH	6	6	6	6
Hydrotrope (Calcium xylene sulfonate)	5	5	5	5
Magnesium^{++} (added as chloride)	3.0	3.0	3.0	3.0
Water and minors	balance	balance	balance	balance
pH @ 10% (as made)	7.5	7.5	7.5	7.5

	E	F	G	H	I	J
pH 10%	9.3	8.5	11	10	9	9.2
MBA13.5E0.6S or MBA13.5S (Example 9)	10	15	10	27	27	20
C25PS	10	0	0	0	0	0
LAS	5	15	12	0	0	0
C26 Betaine	3	1	0	2	2	0
C24 Amine Oxide	0	0	0	2	5	7
LMFAA	3	0	1	2	0	0
C11E8	0	0	20	1	0	2
Hydrotrope	0	0	0	0	0	5
Diamine	1	5	7	2	2	5
Mg++ (as MgCl2)	1	0	0	3	0	0
Ca++ (as Calcium xylene sulfonate)	0	0.5	0	0	0.1	0.1
Protease	0.1	0	0	0.05	0.06	0.1
Amylase	0	0.07	0	0.1	0	0.05
Lipase	0	0	0.025	0	0.05	0.05
DTPA	0	0.3	0	0	0.1	0.1
Citrate	0.65	0	0	0.3	0	0
Water and Minors			(to 100%)			

EXAMPLE 16

The following laundry detergent compositions K to O are prepared in accord with the invention:

	K	L	M	N	O
MBA14.4E0.5S (Example 9)	22	16.5	11	1–5.5	10–25
Any Combination of: C45AS C45E1S LAS C26SAS C47 NaPS C48 MES	0	1–5.5	11	16.5	0–5
QAS	0–2	0–2	0–2	0–2	0–4
C23E6.5 or C45E7	1.5	1.5	1.5	1.5	0–4
Zeolite A	27.8	27.8	27.8	27.8	20–30
PAA	2.3	2.3	2.3	2.3	0–5
Carbonate	27.3	27.3	27.3	27.3	20–30
Silicate	0.6	0.6	0.6	0.6	0–2
PB	1.0	1.0	1.0	1.0	0–3
Protease	0–0.5	0–0.5	0–0.5	0–0.5	0–0.5
Cellulase	0–0.3	0–0.3	0–0.3	0–0.3	0–0.5
Amylase	0–0.5	0–0.5	0–0.5	0–0.5	0–1
SRP 1	0.4	0.4	0.4	0.4	0–1

-continued

	K	L	M	N	O
Brightener 1 or 2	0.2	0.2	0.2	0.2	0–0.3
PEG	1.6	1.6	1.6	1.6	0–2
Sulfate	5.5	5.5	5.5	5.5	0–6
Silicone Antifoam	0.42	0.42	0.42	0.42	0–0.5
Moisture & Minors			Balance		
Density (g/L)	663	663	663	663	600–700

EXAMPLE 17

The following laundry detergent compositions P to T are prepared in accord with the invention:

	P	Q	R	S	T
MBA14.4E0.4S (Example 9)	16.5	12.5	8.5	4	1–25
Any Combination of: C45AS C45E1S LAS C26 SAS C47 NaPS C48 MES	0–6	10	14	18.5	0–20
QAS	0–2	0–2	0–2	0–2	0–4
TFAA	1.6	1.6	1.6	1.6	0–4
C24E3, C23E6.5 or MBA14.5E5 (Example 9)	5	5	5	5	0–6
Zeolite A	15	15	15	15	10–30
NaSKS-6	11	11	11	11	5–15
Citrate	3	3	3	3	0–8
MA/AA	4.8	4.8	4.8	4.8	0–8
HEDP	0.5	0.5	0.5	0.5	0–1
Carbonate	8.5	8.5	8.5	8.5	0–15
Percarbonate or PB1	20.7	20.7	20.7	20.7	0–25
TAED	4.8	4.8	4.8	4.8	0–8
Protease	0.9	0.9	0.9	0.9	0–1
Lipase	0.15	0.15	0.15	0.15	0–0.3
Cellulase	0.26	0.26	0.26	0.26	0–0.5
Amylase	0.36	0.36	0.36	0.36	0–0.5
SRP 1	0.2	0.2	0.2	0.2	0–0.5
Brightener 1 or 2	0.2	0.2	0.2	0.2	0–0.4
Sulfate	2.3	2.3	2.3	2.3	0–25
Silicone Antifoam		0.4	0.4	0.4	0–1
Moisture & Minors			Balance		
Density (g/L)	850	850	800	850	850

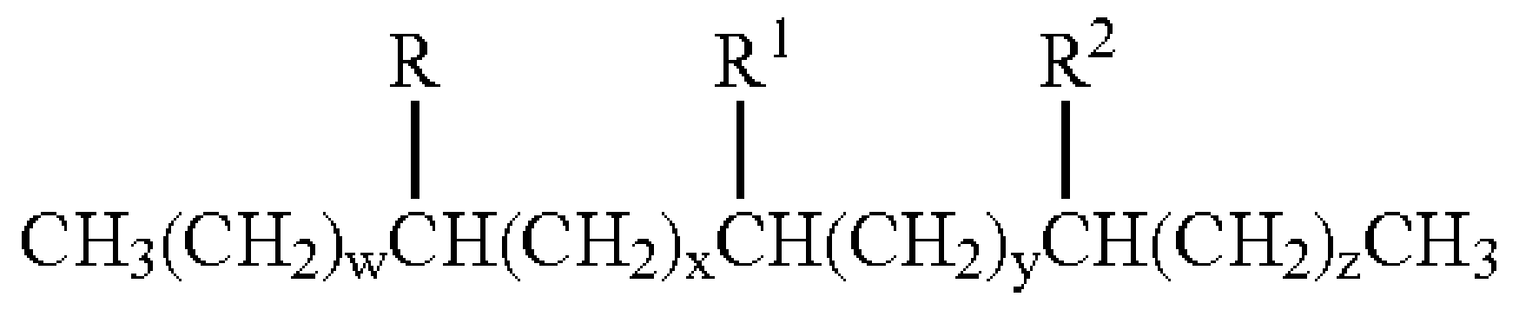
EXAMPLE 18

The following high density detergent formulations U to X, according to the present invention, are prepared:

	U	V	W	X
Agglomerate				
C45AS	11.0	4.0	0	14.0
MBA14.3E0.5S (Example 9)	3.0	10.0	17.0	3.0
Zeolite A	15.0	15.0	15.0	10.0
Carbonate	4.0	4.0	4.0	8.0
PAA or MA/AA	4.0	4.0	4.0	2.0
CMC	0.5	0.5	0.5	0.5
DTPMP	0.4	0.4	0.4	0.4
Spray On				
MBA14.5E5 (Example 9)	5.0	5.0	5.0	5.0
Perfume	0.5	0.5	0.5	0.5
Dry Adds				
C45AS	6.0	6.0	3.0	3.0
HEDP	0.5	0.5	0.5	0.3
SKS-6	13.0	13.0	13.0	6.0
Citrate	3.0	3.0	3.0	1.0
TAED	5.0	5.0	5.0	7.0
Percarbonate	20.0	20.0	20.0	20.0
SRP 1	0.3	0.3	0.3	0.3
Protease	1.4	1.4	1.4	1.4
Lipase	0.4	0.4	0.4	0.4
Cellulase	0.6	0.6	0.6	0.6
Amylase	0.6	0.6	0.6	0.6
Silicone antifoam	5.0	5.0	5.0	5.0
Brightener 1	0.2	0.2	0.2	0.2
Brightener 2	0.2	0.2	0.2	—
Balance (Water/Miscellaneous)	100	100	100	100
Desnity (g/liter)	850	850	850	850

The present process can use many different hydrocarbon feeds, as already illustrated herein. Alternate hydrocarbon feeds that can be used in this process include mixtures of specific types of paraffins and/or mono-olefins. These hydrocarbon mixtures can be selected from:

A. mixtures of paraffins conforming to the formula



$$CH_3(CH_2)_w\overset{R}{\overset{|}{C}}H(CH_2)_x\overset{R^1}{\overset{|}{C}}H(CH_2)_y\overset{R^2}{\overset{|}{C}}H(CH_2)_zCH_3$$

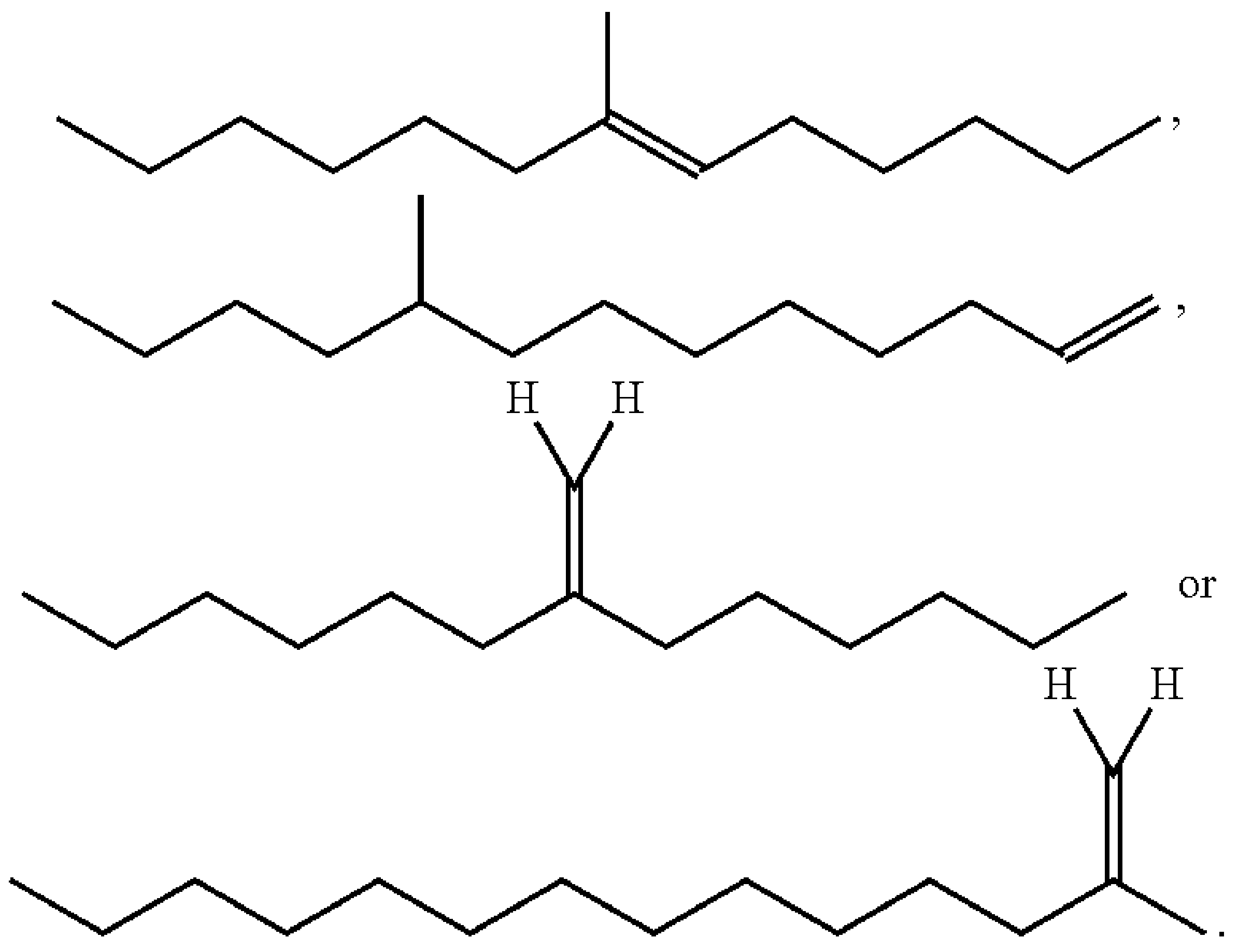
wherein the total number of carbon atoms in the branched primary alkyl moiety of this formula (including the R, R1, and R^2 branching) is from 8 to 20, preferably 10 to 20; preferably from about 10 to about 18; R, R^1, and R^2 are each independently selected from hydrogen, C_1–C_3 alkyl, and mixtures thereof with minor proportions of impurities such as C_3–C_7 cycloalkyl, aryl, arylalkyl and alkaryl, provided preferably from H and C_1–C_3 alkyl (more preferably methyl), provided R, R^1, and R^2 are not all hydrogen and, when z is 0, at least R or R^1 is not hydrogen; w, x, y, z are each independently integers from 0 to 13, subject to the limitation on total carbon number stated supra and w+x+y+z is preferably from 8 to 14.

More highly preferred paraffins have only H, methyl, ethyl, propyl or butyl in R, R^1, and R^2, more preferably only H and methyl, provided R, R^1, and R^2 include at least one alkyl moiety, and methyl, when present, is preferably internal, that is, removed as much as possible from the 1-, 2- and preferably even 3-carbon positions in the longest countable chain.

The hydrocarbons herein also encompass

B. mixtures of mono-olefins. These mono-olefins are related to the paraffins of A above, in that any of the suitable mono-olefins can be made by dehydrogenating any of the paraffins of A. above (In practice, one can first isolate suitable olefins, then hydrogenate them to the paraffins). The preferred olefins are mono-olefins, though in general, up to about 10% by weight of the olefinic hydrocarbon can be diolefins, after dehydrogenation of suitable paraffins.

Like the paraffins, the olefins herein can vary widely in structure, for example, possible mono-olefins are:



These structures are of course illustrative and are not to be taken as limiting

The hydrocarbons herein also encompass:

C. mixtures of the paraffins of A. and the olefins of B. These hydrocarbon mixtures herein can be in any possible combination, and can, for example, be a result of combining compositions containing only paraffins, only olefins, or paraffin/olefin mixtures in any proportion. The mixtures can be derived "inherently" as a consequence of the hydrocarbon coming from a natural, e.g. geologically sourced petroleum raw material (e.g., light crude or kerosene or jet/diesel fuels distilled therefrom), typically with some treatment of such material (for example by fractionation, selective sorption, distillation, clathration etc.) to isolate preferred hydrocarbon mixtures. Alternately, the mixtures can be made up by progressively mixing more complex mixtures from a series of compositionally simple hydrocarbons. The present hydrocarbon mixtures can also derive from any synthetic transformation known in petroleum chemistry, for example cracking, hydrocracking, hydroisomerisation, hydrogenation, dimerization, dehydrogenation, isomerization, disproportionation, and the like. Moreover, equivalent compositions can more painstakingly be built up by means of known organic synthetic schemes, for example those involving Grignard reactions. Catalytic isomerizations on zeolites and modified zeolites can be particularly useful.

Hydrocarbon mixtures useful herein can further include:

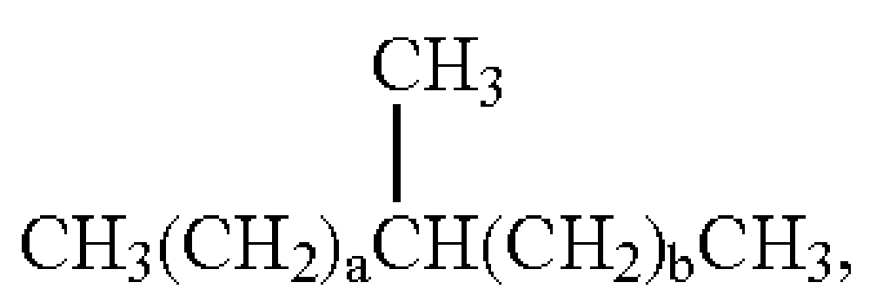
D. mixtures of the paraffins of A. and the olefins of B. with other known olefins and/or paraffins (especially linear ones) in the same or, less preferably, different carbon number range;

And the hydrocarbons herein also encompass:

E. mixtures of A.–D. with benzene or other non-aliphatic hydrocarbons. This includes the use of other solvents such as cyclohexane, pentane, toluene, etc.

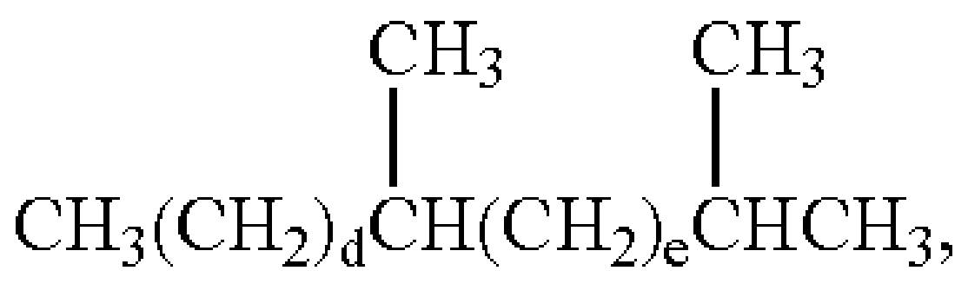
One group of preferred paraffins have the formula selected from:

(II)



$$CH_3(CH_2)_a\overset{\overset{\large CH_3}{|}}{C}H(CH_2)_bCH_3,$$

(III)



$$CH_3(CH_2)_d\overset{\overset{\large CH_3}{|}}{C}H(CH_2)_e\overset{\overset{\large CH_3}{|}}{C}HCH_3,$$

or mixtures thereof; wherein a, b, d, and e are integers, a+b is from 10 to 16, d+e is from 8 to 14 and wherein further

when a+b=10, a is an integer from 2 to 5 and b is an integer from 5 to 8;

when a+b=11, a is an integer from 2 to 5 and b is an integer from 6 to 9;

when a+b=12, a is an integer from 2 to 6 and b is an integer from 6 to 10;

when a+b=13, a is an integer from 2 to 6 and b is an integer from 7 to 11;

when a+b=14, a is an integer from 2 to 7 and b is an integer from 7 to 12;

when a+b=15, a is an integer from 2 to 7 and b is an integer from 8 to 13,

when a+b=16, a is an integer from 2 to 8 and b is an integer from 8 to 14,

when d+e=8, d is an integer from 2 to 7 and e is an integer from 1 to 6;

when d+e=9, d is an integer from 2 to 8 and e is an integer from 1 to 7;

when d+e=10, d is an integer from 2 to 9 and e is an integer from 1 to 8;

when d+e=11, d is an integer from 2 to 10 and e is an integer from 1 to 9;

when d+e=12, d is an integer from 2 to 11 and e is an integer from 1 to 10;

when d+e=13, d is an integer from 2 to 12 and e is an integer from 1 to 11;

when d+e=14, d is an integer from 2 to 13 and e is an integer from 1 to 12.

The present hydrocarbon compositions can accommodate varying amounts of impurities (say tip to about 20%, preferably below about 1%), such as impurities in which one or more ether or alcohol oxygen atoms are present or interrupt the carbon chain(so called "oxygenated" impurities), or impurities in which moieties such as aryl, arylalkyl or alkaryl are attached to the carbon chain as the branches, or impurities in which quaternary carbon atoms are present, or diolefins, or impurities in which nonhydrogen moieties are attached to adjacent carbon atoms. Such impurities are of course not desired. It is especially preferred to limit any impurities known to adversely affect biodegradation or to produce malodors. For greatest mass efficiency, a minimuim of the total carbon content is placed in any of the side-chains, provided that the resulting hydrocarbon preferably still has at least one carbon atom in a side-chain. Preferred paraffins and/or olefins herein may contain varying amounts of non-alkylbenzene aromatic, cycloalkyl and alkyl cycloalkyl impurities, though these are more desirably removed, for example by known sorption steps. Preferred paraffins and/or olefins herein can contain some sulfur and/or nitrogen, but these can produce objectionable odors and for this or other reasons are preferably removed by any of the desulfurization and/or nitrogen removal techniques well known in the petroleum industry.

Preferred olefins are closely related to the paraffins above: they have structures formed by dehydrogenating any of the paraffins in any accessible position to form the corresponding mono-olefin. Especially preferred olefins are monomethyl-branched and dimethyl-branched, particularly monomethyl-branched.

It should be understood and appreciated that the underlying concept being taught for how to select preferred paraffins and olefins for best results herein involves several features including:

(a) making a deliberate selection of mixtures of C10–C18 hydrocarbons having typically one or two alkyl substituents, these preferably being as short as possible, and being positioned at least in a manner consistent with avoiding biodegradation issues. Thus the present hydrocarbons clearly differ substantially from the very non-biodegradable tetrapropylene type; and

(b) preferably having at least some methyl moieties which are not in the 2-position of the longest hydrocarbon chain.

Without intending to be limited by theory, it is believed that some of the more complex mixtures within the defined ranges have especially superior characteristics for forming hydrophobes for highly soluble hardness resistant, cold water tolerant "modified" surfactants including the alkylbenzenes and oxo alcohols.

Additionally, these hydrocarbon mixtures can be broadly used in the production of modified surfactants. They can be used to prepare the modified alkyl sulfates, alkyl alkoxylates, alkylalkoxy sulfates or alkylaryl sulfonates, such as alkylbenzene sulfonates. The alkyl sulfates, alkyl alkoxylates, alkylalkoxy sulfates are prepared by first converting the hydrocarbon mixtures in to the corresponding alcohol and then optionally sulfating and/or alkoxylating the alcohol. The alcohol can be formed by any conventional means, such as by the oxo process. And similarly the sulfation and/or alkoxylation can be by conventional means. The alkylbenzene sulfonates are formed by alkylating benzene with the olefinic containing hydrocarbon mixtures and then sulfonating the resulting alkylbenzene. The alkyl benzene sulfonates formed are the so-called "modified alkyl benzene sulfonate".

What is claimed is:

1. A process comprising:

(A) a stage of at least partially separating a hydrocarbon feed comprising branched aliphatic hydrocarbons having from about 8 to about 20 carbon atoms, into

at least one branched-enriched stream comprising an increased proportion of branched acyclic hydrocarbons relative to said hydrocarbon feed and optionally, one or more of:

a linear-enriched stream comprising an increased proportion of linear aliphatic hydrocarbons relative to said hydrocarbon feed; and

a reject stream comprising cyclic and/or aromatic and/or ethyl- or higher-branched hydrocarbons;

wherein said stage (A) comprises:

providing said hydrocarbon feed; and

adsorptive separation of said feed into said streams using porous media;

said stage (A) using simulated moving bed adsorptive separation means comprising both of:

at least one bed holding said porous media; and

a device for simulating motion of said porous media countercurrent to a hydrocarbon stream in said bed;

(B)

(i) at least partially dehydrogenating the branched-enriched stream of stage (A) thereby forming an olefinic branched-enriched stream comprising mono-olefin, optionally followed by one or more of

(ii) treating said olefinic branched-enriched steam to diminish the content therein of diolefin impurities and

(iii) treating said olefinic branched-enriched stream to diminish the content therein of aromatic impurities;

(C) optionally, at least partially concentrating said mono-olefins in said olefinic branched-enriched stream of stage (B) by means of sorptive separation using a known sorbent or porous media provided that said sorbent or porous media arm nonidentical with the porous media of stage (A) and are adapted for olefin/paraffin separations and, optionally, concurrently recycling paraffins to said dehydrogenation stage (B); and

(D) reacting said olefinic branched-enriched stream produced in stage (B) or, optionally, as further concentrated in stage (C), with carbon monoxide and hydrogen in the presence of an OXO catalyst, thereby forming a modified primary OXO alcohol.

2. A process according to claim **1** meeting at one least one of the following requirements:

said stage (A) means comprise one, two or more of said devices and at least two of said beds, at least one of said beds comprising said porous media differentiated relative to the porous media contents of another of said beds by an increased capacity to retain methyl-branched acyclic aliphatic hydrocarbons; and

said stage (D) is a one-step OXO stage wherein said OXO catalyst is a phosphine-coordinated transition metal other than iron.

3. A process according to claim **2** wherein at least one of said beds comprising porous media conventional for the manufacture of linear alkylbenzenes; said at least one bed having a connection into said process suitable for at least partially increasing the proportion of methyl-branched acyclic aliphatic hydrocarbons in streams passing to said stage (B) of said process, and suitable for at least partially decreasing the proportion of linear acyclic aliphatic hydrocarbons passing to said stage (B) of said process, said linear acyclic aliphatic hydrocarbons being at least partially being removed as said linear-enriched stream in said stage (A).

4. A process according to claim **3** wherein said simulated moving bed adsorptive separation means in said stage (A) comprise

one of said device, provided that said device is capable of simulating movement of said porous media in at least two of said at least one bed; or

at least two of said device.

5. A process according to claim **4** wherein them are two of said at least one bed, each comprising a different member of said porous media, each of said at least one bed being controlled by one of said device, and each of said device having a minimum of eight ports for achieving simulated movement of said porous media in said at least one bed.

6. A process according to claim **4** wherein said linear-enriched stream is present in said stage (A) and said stage (A) comprises:

(A-i) adsorptive separation of said hydrocarbon feed into said linear-enriched stun and an intermediate branched-enriched stream and rejection of said linear-enriched stream by means of one of said simulated moving bed adsorptive separation means; followed by

(A-ii) adsorptive separation of said intermediate branched-enriched stream into said branched-enriched stream comprising an increased proportion of branched acyclic aliphatic hydrocarbons relative to said intermediate branched-enriched stream, and said reject stream comprising at least an increased proportion of cyclic and/or aromatic hydrocarbons relative to said branched-enriched stream, by means of another of said simulated moving bed adsorptive separation means.

7. A process according to claim **2** wherein all of said bed comprises porous media not conventional for the manufacture of linear alkylbenzenes; said porous media having pore sizes suitable for, and being connected into said process, in a manner consistent with at least partially increasing the proportion of methyl-branched plus linear acyclic aliphatic hydrocarbons in streams passing to said stage (B) of said process, and at least partially decreasing the proportion of cyclic, aromatic and/or ethyl-branched or higher, aliphatic hydrocarbons passing to said stage (B) of said process, said hydrocarbons other than said linear- and methyl-branched hydrocarbons being at least partially being removed as a reject stream in said stage (A).

8. A process according to claim **3** wherein said hydrocarbon feed comprises at least about 10% methyl-branched paraffins having molecular weight of at least about 128 and no more than about 282.

9. A process according to claim **3** wherein prior to stage (D) a distillation step is present, whereby said distillation produces a narrow cut of not more than about three carbon atoms in range C10 to C17 in said olefinic branched enriched stream.

10. A process according to claim **9** whereby either said hydrocarbon feed or said olefinic branched enriched stream is subjected to said distillation step.

11. A process according to claim **3** wherein said hydrocarbon feedstock is an adsorptive separation raffinate deriving from a linear alkylbenzene manufacturing process or conventional linear detergent alcohol process.

12. A process according to claim **3** having the additional step or steps in sequence selected from:

(E) sulfating and neutralizing the product of said stage D);

(F) alkoxylating the product of said stage (D); and

(G) alkoxylating, sulfating and neutralizing the product of said stage (D).

13. A process according to claim **12** having the additional stage of (H) mixing the product of the preceding steps with one or more cleaning product adjunct materials; thereby forming a cleaning product.

14. A process according to claim **1** wherein prior to said OXO stage, (D), the product of said stage (B) or (C) is blended with a conventional detergent olefin.

15. A process according to claim **12** wherein the product of any of said stages (E), (F) or (G) are blended with a conventional detersive surfactant.

16. A process according to claim **1** further comprising at least one stage of reacting the product of stage (B) with an aromatic hydrocarbon selected from the group consisting of benzene, toluene and mixtures thereof in the presence of an alkylation catalyst.

17. A process according to claim **16** wherein said alkylation catalyst has an internal isomer selectivity of from 0 to 40.

18. A process according to claim **16** wherein means are provided to route the product of stage (C) to stage (D), or to said alkylation step, or to both of said stages in parallel.

* * * * *